The Dissertation Committee for Rosario Vasquez Scheerhorn certifies that this is the approved version of the following dissertation:

REGIONAL GEOCHEMICAL STUDY OF THE WESTERN INTERIOR PLAINS AQUIFER SYSTEM AND THE GREAT PLAINS AQUIFER SYSTEM IN THE MID-CONTINENT, UNITED STATES

Committee:

Jay L. Banner, Supervisor

John M. Sharp

Libby Stern

Alan Dutton

Alicia Wilson

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by

Rosario Vasquez Scheerhorn, B.A.; M.S.

Dissertation

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

The University of Texas at Austin

August, 2005

Dedication

To my parents and to my husband Jeff

Acknowledgements

I am grateful to my supervisor, Jay L. Banner, for all his support throughout these many years. Committee members, Jack Sharp, Alicia Wilson, Alan Dutton and Libby Stern provided me with insightful comments and questions.

Many individuals have contributed significantly both in the field and in the lab. I am thankful to Lance Christian and Jeff Scheerhorn for their help in the field. To Marylynn Musgrove for her help in the lab, with my paperwork, and support all this many years. I want to thank Larry Mack for his help with the strontium isotopic analysis and mass spectrometry.

I am grateful to numerous oil and gas companies, City of Hays, cattle feeder companies, Sunflower Electric Power Plant, City of Leoti, and United States Air Force Base in Scotts Bluff Nebraska, for allowing us to sample their oil and water wells. Additionally, we want to thank Lance Christian and Jeff Scheerhorn for their help in the field.

I have been blessed with the support of my friends and my family. I want to specially thank my husband, Jeff, for helping me get through this process and supporting me all this years.

REGIONAL GEOCHEMICAL STUDY OF THE WESTERN INTERIOR PLAINS AQUIFER SYSTEM AND THE GREAT PLAINS AQUIFER SYSTEM IN THE MID-CONTINENT, UNITED STATES

Publication No._____

Rosario Vasquez Scheerhorn, Ph. D

The University of Texas at Austin, 2005

Supervisor: Jay L. Banner

A wide range of chemical and isotopic variability characterizes the Great Plains Aquifer System (GP) and the Western Interior Plains Aquifer System (WIP), reflecting a range of fluid mixing processes and water:rock interaction. The study area extends 1200 km from eastern Colorado to central Missouri and from Nebraska to the Oklahoma panhandle. The GP comprises Cretaceous sandstones that are both overlain and underlain by shales. The WIP comprises carbonates and sandstones of Cambrian through Mississippian age. This aquifer system underlies Pennsylvanian through Jurassic shales and overlies the Precambrian basement.

The WIP groundwater has been classified into three distinct groups; Group 1 is a fresh water originating in the Ozark Plateau, Group 2 is a saline groundwater possibly originating in the Colorado Front Range, and Group 3, originating in the Anadarko Basin, is the most saline groundwater of the three. Results from fluid mixing models suggest that the groundwater in the WIP can be explained by the

mixing between these three groundwater groups. The salinity of the WIP could be the result of two different mechanisms, halite dissolution and evaporation of seawater.

The GP groundwater can be divided into two groups; GP1 is a fresh groundwater present in the unconfined portion of the aquifer while GP2 is a saline groundwater present in the confined portion of the aquifer. GP2 groundwater acquired its salinity from interaction with groundwaters upwelling from the Permian shales and evaporites. The strontium isotopic composition of GP2 also implies that these groundwaters have mixed with groundwater migrating upwards from the Pennsylvanian shales. The light isotopic signature of both GP1 and GP2 suggests that this groundwater recharged at higher elevations and colder climatic conditions in the Colorado Front Range. Fluid-mixing modeling results between the two groundwater types suggest that the groundwater from the confined system and the groundwater from the unconfined system are not mixing.

Table of Contents

List of Tables

List of Figures

CHAPTER 1

INTRODUCTION

Introduction

There is great uncertainty regarding the extent of regional scale flow systems and there is still controversy over the mechanisms that generate saline fluids in sedimentary basins. This study investigates the hydraulic continuity of the Western Interior Plains aquifer system (WIP), the origin and evolution of the groundwaters in the WIP, the origin and evolution of the groundwater in the overlying Great Plains aquifer system (GP), and the mechanisms that generated the salinity in both the WIP and the GP.

Large-scale flow systems are important because they control processes of ore genesis, migration of oil and gas, metamorphism, and diagenesis (Gunter et al., 2000). Regional flow systems are also important sources of freshwater and potential repositories for hazardous waste materials and greenhouse gases such as carbon dioxide (Bachu et al., 2000, Horita et al, 2001, Cathles, 1990). The WIP in the mid-continent exhibits extreme chemical and isotopic variations that suggest large scale fluid flow, fluid mixing processes and different mechanisms for the generation of saline fluids (Musgrove and Banner, 1993). The interaction of all the mentioned processes and variations makes the WIP a well suited aquifer system to test the hypothesis of hydraulic continuity.

Organization

This dissertation consists of five chapters. Chapter 1 provides an introduction to the study, a summary of the different chapters, and some background information on the study area. The following chapters are written as

stand-alone journal articles. Chapter 2 addresses the issue of continental scale flow in the Western Interior Plains Aquifer system (WIP). Chapter 3 discusses the origin and evolution of the groundwaters in the WIP. Chapter 4 focuses on the origin and evolution of the groundwaters in Great Plains aquifer system (GP). Chapter 5 is a conclusion chapter that presents the main results from Chapters 2, 3, and 4.

Chapter summaries

Chapter 2 – A Continental-Scale Groundwater Flow System

This chapter focuses on evaluating the existence and extent of regional scale flow systems. There are very few examples of modern of regional scale flow systems. This study, using geochemical and isotopic tools, investigates the possibility of hydraulic continuity at a 1200 km-scale in the WIP. Over this areal extent, three distinct groundwater endmembers were identified. Endmember 1, a dilute water originating in the Ozark Plateau, Endmember 2, a saline groundwater possibly originating in the Colorado Front Range, and Endmember 3, the most saline groundwater, originating in the Anadarko Basin. Results of fluid mixing models suggest that the groundwater in the WIP is the result of mixing between these three endmembers. The regional extent of these geochemically and isotopically distinct endmembers suggest that the WIP is a continuous flow system extending over eastern Colorado, Kansas, eastern Missouri, and northern Oklahoma.

Chapter 3 – The Origin and Evolution of Saline Groundwater in the Western Interior Plains Aquifer System (WIP), Mid-Continent, United States

This chapter addresses the origin and evolution of the saline groundwaters in the WIP. Two different mechanisms for the origin of the saline fluid, dissolution of evaporites and evaporation of seawater, were evaluated using the relationships between Br/Cl and Br/Na, Ca_{excess} and $Na_{deficit}$, cation and anion data, and both stable isotopes of H and O, together with strontium isotopic values. The origin of the salinity for Group 2 was found to be due to the dissolution of evaporites, subsequently modified by water:rock interaction. The possible sources are Permian evaporites, either the Wellington Formation or the Nipewalla Group. The salinity for Group 3 is possibly due to the evaporation of seawater and subsequent water-rock interaction. Strontium isotope values for Group 2 are higher than values for Paleozoic seawater, suggesting that these waters have experienced extensive water:rock interaction. Possible sources of this radiogenic strontium in central Kansas could be interaction of WIP groundwater with Precambrian granite along the Central Kansas Uplift or the Nemaha Uplift, mixing with fluids that have been in contact with overlying Pennsylvanian shales.

Chapter 4 – Regional Geochemical and Isotopic Study of the Great Plains Aquifer System (Dakota Aquifer) in Kansas, Nebraska, and Colorado

Chapter 4 describes the geochemistry and isotopic composition of groundwater in the GP aquifer in the mid-continent. The GP aquifer system

extends from New Mexico to the Artic Circle in Canada (Gosslin, 2001). This aquifer system provides water for agricultural and municipal purposes. The groundwater in the GP can be divided into two groups according to their geochemical and isotopic character. GP 1 is dilute groundwater present in the unconfined portion of the aquifer in Kansas, and in the confined portion of the aquifer in northeastern Colorado and northwestern Nebraska, and GP2 is saline groundwater present in eastern Colorado and western Kansas. Both GP1 and the GP2 groundwater fall along the Meteoric Water Line, suggesting a meteoric origin for both of them. H and O isotopic variations for GP1 and GP2 suggest that these groundwaters were recharged at high altitude, with the potential influence of colder climatic conditions. These groundwaters likely acquired their salinity from mixing with fluids that have been in contact with evaporites. Strontium isotope values for GP2 are radiogenic, suggesting that these groundwaters have been in contact with a silicate source, such as underlying Pennsylvanian shales.

Chapter 5 – Summary and Conclusions

The extent of the three groundwater groups in the mid-continent suggests that the WIP is hydraulically connected throughout the mid-continent. Three distinct groundwater types are identified in the mid-continent, each with an origin in different geographic locations. Fluid mixing exerts a significant control over the geochemical and isotopic character of the three different groundwater groups present in the WIP. Water:rock interaction has altered the strontium isotopic

signature of Groups 2 and 3, suggesting that fluids that have been in contact with Pennsylvanian shales or Precambrian basement. Two different mechanisms for generating saline fluids were recognized in the WIP, dissolution of evaporites and evaporation of seawater.

Two different water types are recognized in the GP. Groundwaters in western and Kansas and eastern Colorado, both in the confined and unconfined portion of the GP, have very low H and O stable isotope signatures. This water could have been recharged at high altitude during colder climatic conditions. The salinity in GP groundwater is the result of these groundwaters mixing with fluids that have been in contact with the Permian evaporites. There are a few samples in eastern Colorado that exhibit a very high strontium isotopic composition, which could be the result of interaction with Pennsylvanian shales or shales from the GP confining system.

A suite of different geochemical and isotopic factors were used to determine origin and evolution of the groundwaters in the GP and the WIP. H and O isotopic values were used to determine the origin of the groundwaters and to suggest processes that might be affecting the groundwater. Na-Ca-Br-Cl were used to determine the origin of the salinity. Strontium isotopes helped determine the extent of water:rock interaction. Mixing processes were determined using the modeling results from H and Cl models.

CHAPTER 2

A CONTINENTAL-SCALE GROUNDWATER FLOW SYSTEM

Abstract

Our understanding of regional scale flow systems is important because they control major geological process. Modern analogs of regional scale flow systems are rare. The Western Interior Plains aquifer system (WIP) in the mid-continent, U.S.A., has been proposed to be hydraulically continuous from the Colorado Front Range to eastern Missouri. This study applies geochemical and isotopic variations present in this regional aquifer to ascertain the scale of hydraulic continuity in the WIP. Three distinct groundwater endmembers have been identified in the WIP, a fresh dilute water originating in the Ozark mountains, a saline groundwater originating in the Colorado Front Range, and a saline groundwater originating the Anadarko Basin. Fluid mixing modeling suggests that the groundwaters in the WIP at a 1200 km scale are the result of mixing between the three endmembers. The regional extent of these geochemically and isotopically distinct endmembers suggests that the WIP is a continuous flow system extending over eastern Colorado, Kansas, eastern Missouri, and northern Oklahoma.

Introduction

A major uncertainty in the Earth sciences is determining the existence and the spatial extent of regional groundwater flow systems. Such systems control processes of ore genesis, migration of oil and gas, metamorphism, and

diagenesis (Gunter et al., 2000). Regional flow systems are also important sources of freshwater and potential repositories for hazardous waste materials and greenhouse gases such as carbon dioxide (Bruant et al., 2002).

Regional-scale groundwater flow systems have been proposed as being active in the past yet modern examples are rare. An example of a modern analog is the 800 km long Great Artesian Basin in Australia (Calf and Habermehl, 1993). Due to the limited amount of modern systems that have been recognized and studied, our understanding of continental-scale flow systems is still in its infancy. Regional flow in the past is implicated in the formation of heavy oil deposits in Paleozoic carbonates and Mesozoic sands in the Western Canada Basin (Garven, 1985). It is theorized that the post-Laramide uplift of the Western Canada Basin triggered the creation of a topography-driven hydrodynamic system capable of transporting large volumes of water across the basin (Garven, 1989). In the mid-continent United States, some paleo-brine migrations may have occurred within giant hydrothermal systems that operated on regional scales up to 700 km (Bethke and Marshak, 1990). It has been proposed that a west-to-east gravity-driven flow system in the mid-continent, the Western Interior Plains aquifer system (WIP), is driven by recharge in the Colorado Front Range and extends 1200 km across the mid-continent to Missouri (Jorgensen, 1989). The WIP is hypothesized to transmit saline and fresh groundwater on this large scale and to have developed as a result of the Laramide orogeny 65 million years ago (Jorgensen, 1989). These hypotheses and models pose several fundamental questions. Is the WIP a regional-scale groundwater flow system or an aggregate

of smaller isolated flow systems? What are the sources of recharge and processes by which saline and fresh groundwaters in the WIP have evolved? The scales over which hydraulic continuity exists in aquifers are uncertain, yet this information is essential to understanding groundwater migration and many other Earth science processes.

The present study applies geochemical and isotopic variations in WIP groundwater to ascertain the scale of hydraulic continuity of regional-scale flow system. Three distinct geochemical groundwater groups are identified in the WIP. Systematic spatial variations of major ion concentrations, stable isotope ratios, and geographic distribution of these three groups on a 1200 km scale were found. Quantitative fluid mixing models can account for the regional differences in groundwater composition of these groups. The geographic distribution of the groundwater groups is consistent with the WIP being a continuous regional-flow system (Fig. 2.1A).

Approaches to determining scales of hydraulic continuity

At a local scale, the continuity of a groundwater flow system can be tested using introduced tracers such as dyes and various ions, as well as naturally occurring tracers such as elemental concentrations and stable and radiogenic isotopes. Deep regional aquifers tend to exhibit low permeability and porosity due to the burial and compaction of their constituent strata and, consequently,

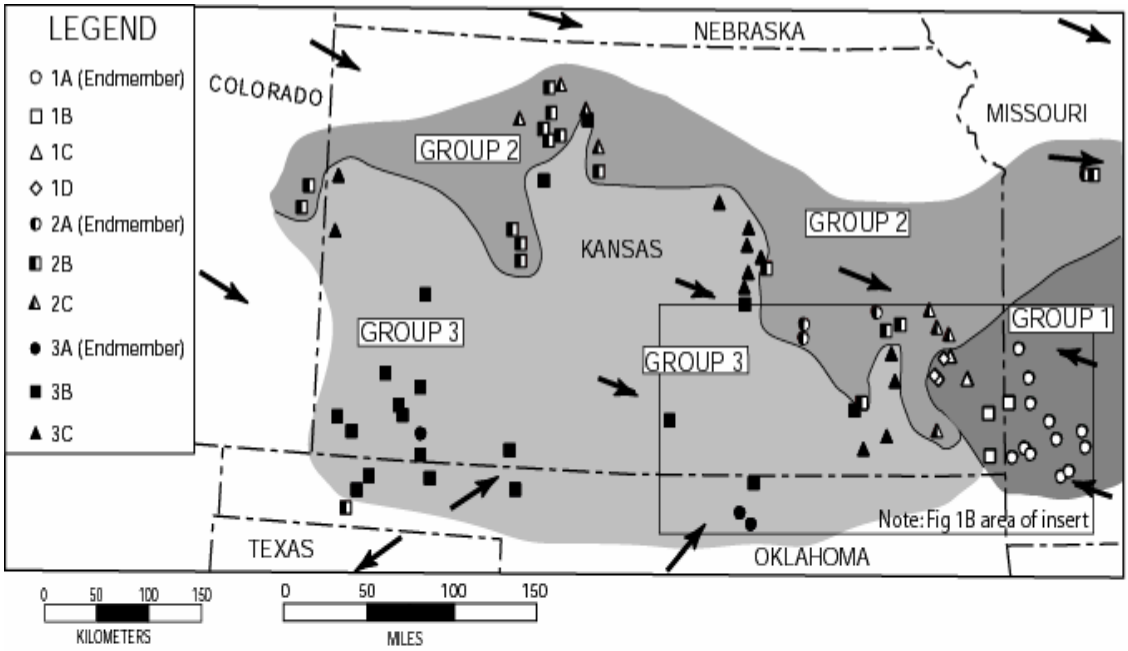
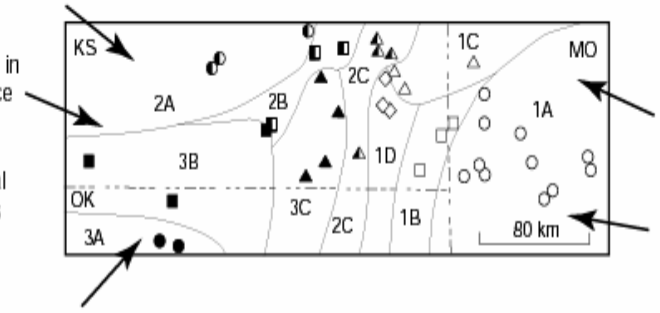


Fig. 2.1A Close up of the study area showing group location and regional extent of groundwater groups from the Western Interior Plains Aquifer system. The regional extent of the groups is based on sample localities and geochemical characteritics. Data from Musgrove and Banner (1993), Nicastro (1983), Chaudhuri (1987, 1992), and from this study. Arrows represent regional groundwater flow patterns based on data in Larson (1971), Jorgensen (1989) and Jorgensen et al (1986). Groundwaters were obtained from water wells and oil/gas wells. Water wells are present in southwestern Missouri and southeastern Kansas only, the remainder of the groundwaters were obtained from oil/gas wells.

Fig. 2.1B Close up of study area from Musgrove and Banner (1993). In this area in the mid-continent there is a correspondence between flow direction, geography, and chemistry and stable isotopes. The same correspondence is not observed in regional scale (fig. 1A). Positions of boundary lines are based on sample localities and geochemical characteristics. Arrows represent regional flow direction.



testing the continuity of these aquifers with introduced tracers requires a long period of time and/or an innovative approach.

Stable isotopes of hydrogen and oxygen in water can be used to determine regional groundwater flow direction and areas of recharge (Mazor, 1991). Deuterium and oxygen isotopes vary as a function of the amount of rainfall, temperature, altitude, evaporation, and distance from the ocean, and

these variations can be used to infer recharge areas and flow paths (Davis et al., 1985). Chloride and bromide have been used as groundwater tracers; these anions as well as hydrogen isotopes usually behave conservatively during processes of water:rock interaction involving carbonates and silicates, and are thus well suited to trace groundwater mixing (Banner et al., 1994). Radiogenic isotopes, such as strontium isotopes, can be used to trace sources of dissolved constituents in groundwater and the compartmentalization of subsurface reservoirs (Mearns and McBride, 1999 and Calf and Habermehl, 1983). Other isotopes, such as chlorine-36 and carbon-14, can be used to estimate direction of flow within an aquifer (Mazor, 1991).

Human-introduced tracers include those introduced intentionally, such as dyes, and tracers that have been introduced unintentionally, such as chlorofluorocarbons (CFCs) and tritium. CFC's are anthropogenic organic compounds that have been produced since the 1930's and are used for a variety of domestic and industrial purposes (Solomon et al., 1998). Both CFC's and tritium can be used as tracers of groundwater and as age dating tools in young aquifer systems, i.e. 50 to 70 years. Human-introduced tracers have been used to test continuity at a local scale, but cannot be used to test continuity in regional systems, since the groundwater transport time across these systems is prohibitively long and dispersivity is too large. The geochemical tracers described in this section have been used successfully at different scales to determine the continuity of other flow systems, such as the Kobio aquifer in Niger, Lower Jurassic N aquifer in Black Area Mesa, Arizona and the Great

Artesian basin in Australia (Bentley et al., 1986; Calf and Habermelh, 1983, Girard et al., 1997, and Lopes and Hoffman, 1997).

Tracing continuity: Case studies

The continuity and groundwater recharge sources of the Kobio aquifer, in Niger, at a 3 km scale were determined using stable isotopes, tritium ages, and hydrogeological information, such as recharge areas and groundwater flow velocity (Girard et al, 1997). Using the same geochemical tools used in the Kobio aquifer study, together with major ion chemistry and radiogenic isotopes, researchers determined the flow direction and recharge area of the Lower Jurassic N aquifer in Black Area Mesa, Arizona (Lopes and Hoffman, 1997). The results of the Lower Jurassic N aquifer study showed that groundwater flows south-southeast from the recharge area into the confined area of the aquifer over a distance of 100 km. These tracers have also been used successfully on larger scale flow systems such as the Great Artesian Basin.

The Great Artesian Basin in Australia extends 800 km west to east and occupies 1.7×10^6 km^2 (Calf and Habermehl, 1983). Recharge areas and regional groundwater flow patterns of the aquifer were determined using ^{14}C, ^{36}Cl, and $^{13}C/^{12}C$ and major-ion chemistry of the groundwater (Calf and Habermehl, 1983). The regional groundwater movement in the basin was also determined from potentiometric surface maps. Results from the ^{36}Cl studies indicate a general agreement between the hydrologic-model ages and the

radioisotopic-model ages, suggesting that flow conditions have not changed significantly over approximately one million years (Torgensen et al., 1991 and Bentley et al., 1986).

Few examples of regional scale flow systems, such as the Alberta Basin (540 km) in Canada and the Great Artesian Basin (800 km) in Australia (Calf and Habermehl, 1983, Bachu, 1995, and Tóth, 1995) have been identified. The extent of hydraulic continuity in regional scale groundwater systems is poorly understood. This could be due, in part, to the rarity of cases where these hydraulic extents are tested. The present study evaluates the hypothesis that the WIP is a regional groundwater flow system with hydraulic continuity over 1200 km in the mid-continent, USA (Jorgensen, 1989).

Western Interior Plains aquifer system (WIP)

The Western Interior Plains aquifer system lies within the presently tectonically stable interior of the North American craton and is characterized by continuous time-stratigraphic rock formations locally interrupted by major, sub-vertical fault zones and structural arches. The WIP consists of dolomites, limestones, and sandstones of Cambrian through Mississippian age. This regional aquifer is overlain by the Western Interior Plains confining system and underlain by Precambrian basement (Fig. 2.2). The WIP confining system consists of rocks of Upper Mississippian through Jurassic age, but is mostly Pennsylvanian and Permian shales and evaporites (Signor and Imes, 1988).

The intrinsic permeability of these rocks, which is greatly affected by depth and compaction, ranges from 10^{-18} ft^2 to 10^{-12} ft^2 ($9.3x10^{-19}$ m^2 to $9.3x10^{-13}$ m^2). The regional values for porosity range from 1% to 5% (Jorgensen et al. 1993). Groundwater moves very slowly from west to east due to the very low intrinsic permeability and minimal hydraulic gradient (Jorgensen et al., 1993). Since the onset of the Laramide Orogeny, 65 Ma, there has been sufficient topographic relief to generate flow from west to east, from the Colorado Front Range to Missouri. In order for groundwater to travel 1200 km in 65 million years, flow rates in excess of 0.015 m/y are required. Results of computer simulations of regional flow indicate that in some areas of the WIP flow can be as slow as 1.2 x 10^{-5} m/y (Signor, 1988). Using the Signor's (1988) flow rate of 1.2 x 10^{-5} m/y , and assuming that groundwater traveled 1200 km in 65 million years, would result in brines that are more than 100 million years old. This variability in flow velocity within the WIP suggests the aquifer does not behave as a uniform porous media.

Results

The WIP extends 1200 km west to east from the Colorado Front Range to eastern Missouri and about 500 km north to south from the Nebraska Panhandle to the Oklahoma Panhandle (Musgrove and Banner, 1993, Fig. 2.1A). In order to ascertain the continuity of the WIP in the mid-continent, fifty-four groundwater

samples were collected from oil, gas, industrial and municipal wells during August 1997 and October 1998.

Groundwaters from the WIP exhibit a wide range of elemental and isotopic compositions. The range of salinity in the WIP is extreme, ranging from 200 mg/l to 246,500 mg/l. The isotopic composition of oxygen and hydrogen of the groundwater in the WIP ranges from -10.9‰ to 1.3‰ and -83‰ to -16‰ for $\delta^{18}O$ and δD values, respectively. The predominant constituents in the WIP groundwater are Na, Cl, Ca, and SO_4. Based on isotopic and geochemical data,

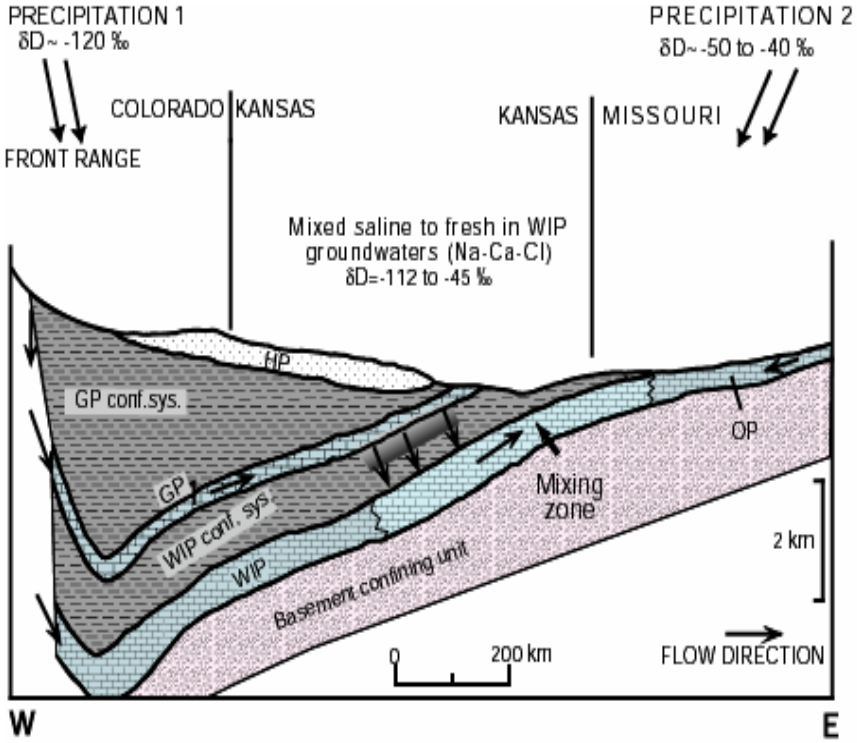


Fig. 2.2 Cross-section cartoon of the Midcontinent aquifer systems. WIP stands for Western Interior Plains aquifer system, GP for Great Plains aquifer system, HP for High Plains aquifer system, OP, for Ozark Plateaus aquifer system. The arrows within the Western Interior Plains confining system represent saline cross-formational flow. Diagram modified from Banner et al., 1989 and Jorgensen, 1989.

Table 2.1 Mean geochemical and isotopic values for the Western Interior Plains aquifer system and the Great Plains aquifer system in the mid-continent.

Group	Members	TDS mg/l	$\delta^{18}O$ per mil	Cl mg/l
1	1A*	370	-6.2	9.50
	1B	660	-6.6	53.3
	1C	2,500	-6.5	1,100
	1D	11,500	-6.3	6,300
2	2A*	26,200	-13.5	14,700
	2B	39,800	-9.4	21,400
	2C	45,100	-6.6	25,600
3	3A*	238,800	2.6	176,900
	3B	192,600	-1.2	109,800
	3C	84,100	-5.2	52,100
GP1	GP1*	1,000	-12.2	110
GP2	GP2*	28,400	-9.4	14,700

Data are from Musgrove and Banner (1993), Nicastro (1983), Chaudhuri (1987, 1992), Dutton (1994), and this study. Values represent the calculated mean for each group. TDS = calculated total dissolved solids. $\delta^{18}O$ values are relative to Standard Mean Ocean Water. Members with an asterisk represent the endmembers for that group.

Group 2 is predominately a Na-Ca-Cl groundwater and has δD and $\delta^{18}O$ values varying from –100 ‰ to –50 ‰ and –14 ‰ to –4 ‰, respectively. Group 3 is the most saline group and has the highest δD and $\delta^{18}O$ values ranging between –66 ‰ to –5 ‰ and –7 ‰ to 3 ‰, respectively. These waters are Na-Ca-Cl brines with salinities ranging between 62,300 mg/l to 246,500 mg/l.

Discussion

I hypothesize that the WIP is a continuous regional-scale flow system extending over parts of Colorado, Kansas, Missouri, and Oklahoma. This

hypothesis is tested here by correlating the geochemical origin and evolution of these groundwaters and then integrating these correlations with spatial geochemical variations. On the basis of groundwater geochemical and isotopic variations, I propose that there are three distinctly different groundwater groups present in the WIP. The geochemical variations indicate different origins and evolution pathways for each group.

Sources of recharge for Endmember 2

The stable isotopic composition of the groundwaters is dependant on temperature (seasonality or changes in climate), altitude, water:rock interaction, and continentality (Mazor, 1991). The continental effect occurs when isotopic composition of the precipitating air masses becomes gradually lighter as it moves inland (Mazor, 1991). The changes in magnitude of the continental effect that may occur between glacial and interglacial conditions are likely overshadowed by the magnitude of the effects of changing temperature and seawater $\delta^{18}O$ values. Based on the very low δD and $\delta^{18}O$ isotope values of the groundwater, I propose that Endmember 2 originates at high altitudes during colder climatic conditions in the Colorado Front Range and migrates into the study area where it mixes with groundwater from Groups 1 and 3. Colder climatic variations alone do not explain the low isotopic signature observed in Endmember 2. In order to obtain a 6-9‰ shift observed between Endmember 2 $\delta^{18}O$ values and present day local recharge $\delta^{18}O$ values in central Kansas, however, the mean annual air temperature at the time of recharge would have to have been 10-14°C cooler

than present day (Dansgaard, 1964). This exceeds the calculated estimates of maximum ice-age surface temperature for Antarctica and Greenland, which are on the order of 8-9°C cooler than today (Broecker and Denton, 1989). The temperature variations for the mid-continent have been estimated to be 4-5°C cooler than present day (Webb and Bryson, 1972 and Yapp and Epstein 1977).

An alternate explanation for the low isotopic signature of Endmember 2 could be recharge by glacial meltwaters (Siegel and Mandel, 1984 and Siegel, 1989). However, geographic variations in groundwater chemistry and patterns and rates of groundwater flow make the glacial meltwater recharge model unlikely (Banner et al., 1989, Jorgensen et al., 1986, and Signor and Imes, 1988).

Stable isotopes of oxygen and deuterium, together with major ion chemistry, are used to evaluate the extent of continuity in the Western Interior Plains aquifer system on a 1200-km scale (Fig 2.1A). Data collected as part of this study were analyzed together with data from previous, more localized studies in the mid-continent (Musgrove and Banner, 1993, Banner et al., 1989, Chaudhuri et al., 1987, Chaudhuri et al., 1992, and Nicastro, 1983).

Fluid mixing models

Chloride concentrations and δD values are among the most conservative parameters in groundwater during the processes of water:rock interaction involving carbonates and silicates. Their conservative nature makes these parameters particularly well suited to ascertain the processes of fluid mixing.

Mixing models simulate processes that can account for the observed range in the geochemical and isotopic variations. Modeled mixing curves are based on mass-balance relationships (Banner et al., 1989). The three different groundwater groups identified in the WIP are apparent in a δD-Cl space (Figs. 2.3A and 2.3B). The correspondence of the model curves and the groundwater data suggest that mixing in the WIP at a 1200 km-scale involves all three endmembers (Fig. 2.3C). The systematic geographic variations of δD and Cl indicate that the groundwater in the WIP has distinct origins (Figs. 2.1A and 2.3B). The same large extent of geochemical and isotopic variability in the groundwater was observed at a 250 km scale in northwest Oklahoma, southwest Missouri and southeast Kansas (Musgrove and Banner, 1993).

Fluid-mixing modeling and major-ion concentrations suggest that groundwaters in the mid-continent at a 1200 km- scale are the result of mixing between Endmembers 1, 2 and 3 and an additional dilute endmember. Evaluation of regional groundwater flow direction shows that Endmember 1 cannot be the freshwater component for central and western Kansas, northwestern Oklahoma, and eastern Colorado, since Endmember 1 groundwater does not occur further west than southeast Kansas (Fig. 2.1A). An alternative freshwater endmember could be fresh water from the Great Plains aquifer system (GP). The GP, also known as the Dakota aquifer, overlies the WIP confining system (Fig. 2.2). In general in the GP, flow is from west-southwest to east-northeast. The GP can be divided into two distinct groups

according to their geochemical and isotopic signatures. Both GP1 and GP2 were used as endmembers (Fig. 2.3C).

In order for GP groundwater to be an endmember in fluid mixing processes in the WIP, water would have to infiltrate across Pennsylvanian shales. It has been observed that, in general, the hydraulic potential of the Pennsylvanian strata is higher than those of the lower strata (Belitz and Bredehoeft, 1988 and Larson, 1971). This differential in potential allows a downward flow through the confining units into the WIP, i.e. flow from high potential to low potential. This downward flow is probably through a combination of both diffusive transport and advective transport along fractures and preferential migration pathways.

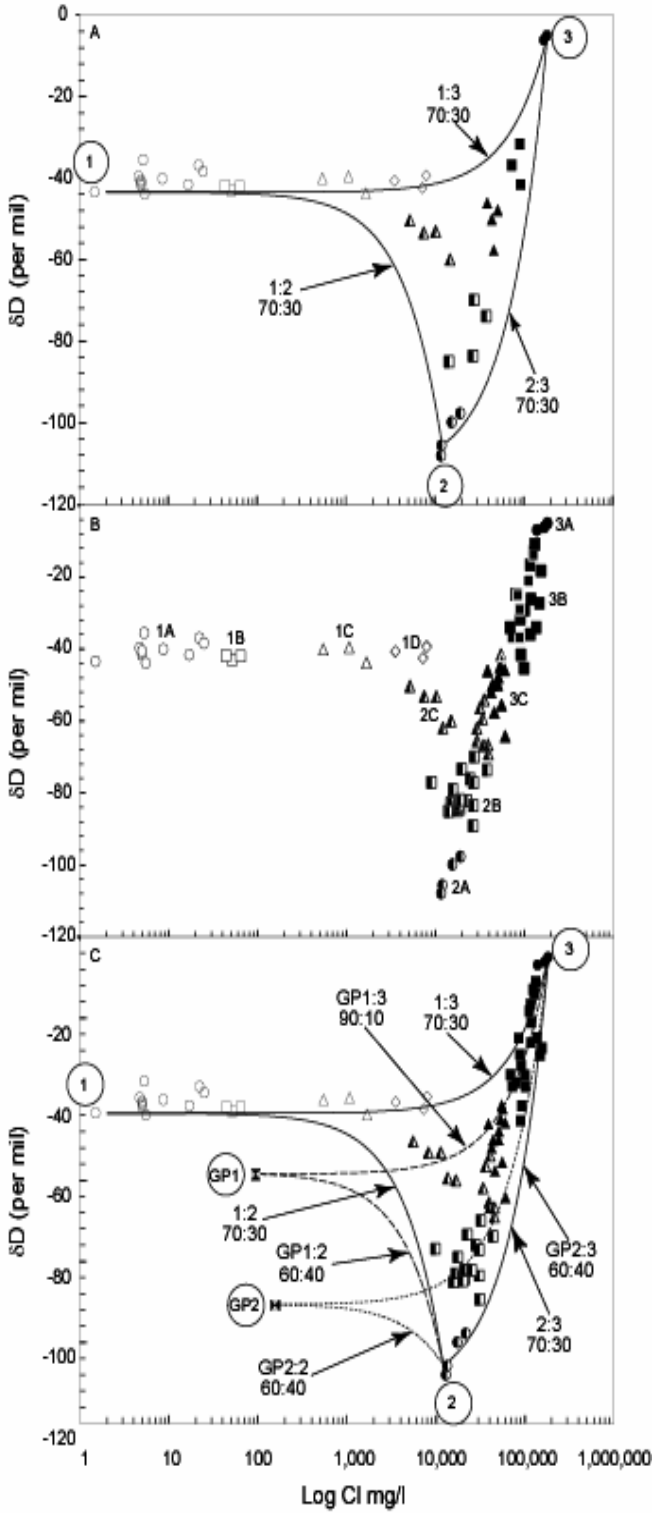
Stable isotopes constraints on the origin of Endmembers 1, 2, and 3

Oxygen and hydrogen isotopic compositions of the groundwaters from south-central Kansas, southwest Kansas, eastern Colorado, and the Oklahoma Panhandle, together with results from other studies (Musgrove and Banner, 1993, Banner et al., 1989, Chaudhuri et al., 1987, Chaudhuri et al., 1992, and Nicastro, 1983), were compared to the Meteoric Water Line (Fig. 2.4). The

Fig. 2.3 (A) δD vs Cl concentrations for Musgrove and Banner (1993), with Cl concentrations depicted on a logarithmic scale to illustrate the extent of group 1 samples. Open symbols corresond to group 1, half filled symbols to group 2, and filled symbols to group 3. Group endmembers are identified by circles. Curves depict the results of mixing models between Endmembers 1, 2, and 3. Other geochemical variations such as dD

Fig.2.3(B) Same as fig. 2.3A without the mixing curves and incorporating groundwaters from south-central Kansas, eastern Colorado, and the Oklahoma pandhandle. Note that the samples fall within the same chemical and isotopic groups as the samples from Musgrove and Banner (1993). Group identification is the same as Fig. 2.3A.

Fig. 2.3(C) Same as (B). Curves depict the results of mixing modeling involving Endmembers 1, 2, 3, GP1, and GP2. The extent of Endmember 1 is limited to southeast Kansas and southwest Missouri making it impossible for this endmember to be the fresh dilute endmember mixing with endmembers 2 and 3 in the rest of the study area. Groundwater from the Great Plains Aquifer system (GP1 and GP2) was used as an alternate fresh dilute endmember in this mixing model. GP1 endmember is depicted



Meteoric Water Line (MWL) represents the linear relationship between δD and δ^{18}O in precipitation from locations around the globe. It is a convenient reference line for understanding and tracing groundwater origins and movements (Mazor, 1991).

Both Endmember 1 and 2 samples plot along the Meteoric Water Line. The signature of Endmember 1 is similar to the signature of local modern precipitation in Missouri, suggesting that this groundwater is derived from local recharge to the Ozark Plateaus aquifer system. The low δD and δ^{18}O values and high salinities exhibited by Endmember 2 are anomalous in comparison to the trend commonly observed in saline groundwaters from other basins. Increasing groundwater salinity is often correlated with increasing deviation from the Meteoric Water Line, which reflects the effects of evaporation (Clayton et al., 1966 and Hitchon and Friedman, 1969). The hydrogen and oxygen isotopic values of Endmember 2 are similar to those of modern meteoric precipitation in the Colorado Front Range (Musgrove and Banner, 1993), suggesting that this endmember could have recharged during colder climatic conditions and at higher elevations.

Group 3, which comprises the most saline groundwaters, has the lowest δD and δ^{18}O values. The H and O isotopic values for Group 3 are similar to those found in other basinal saline fluids, where salinity increases with increasing deviation from Meteoric Water Line (Hitchon and Friedman, 1969). Hydrogen and oxygen values similar to those from Group 3 have been observed in brines resulting from the evaporation of seawater (Holser, 1979).

Hydraulic continuity

On a regional scale, Group 1 is present in southwest Missouri and southeast Kansas, Group 2 is present in northern Colorado, Kansas, and Missouri, and Group 3 present in southern Kansas, and northern Oklahoma (Fig. 2.1A). The geographic distribution of these geochemical groups appears to be controlled by the regional-groundwater flow direction of the Western Interior Plains aquifer system (Fig. 2.1A). Analysis of the potentiometric surfaces of the WIP is consistent with Group 3 groundwaters originating in the Anadarko basin (Burrus and Hatch, 1989). The results of organic geochemical analysis of hydrocarbons in the Anadarko Basin and southern Kansas also support the idea of long distance migration from the Anadarko basin into south-central Kansas (Jorgensen et al., 1986a). Geochemical and isotopic data from Group 1 indicates that this groundwater represents meteoric recharge to the Ozark Plateaus aquifer system. Present-day groundwaters in the Ozark Plateaus system flow in a radial pattern from the Ozark dome and westward toward the study area. Hydrogen and oxygen isotopic values of modern precipitation on the Colorado Front Range are similar to those observed in Group 2. This suggests that Group 2 groundwater could be recharged in the Colorado Front Range before traveling about 1200 km to central Missouri. It can be observed in figure2.1 that Endmember 2 was not found close to the Colorado Front Range.

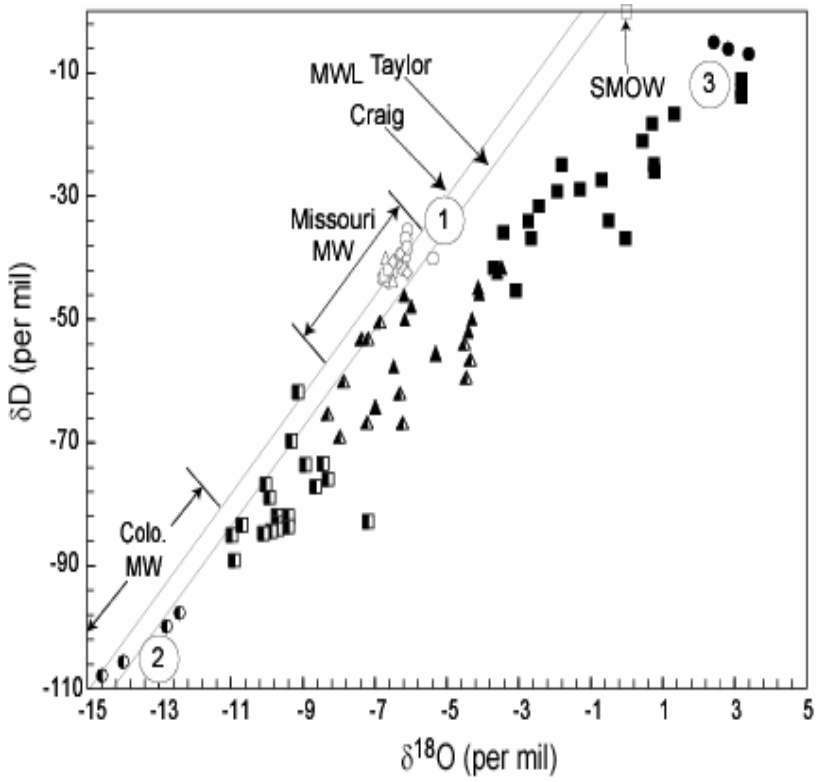


Fig. 2.4 δD versus $\delta^{18}O$ for groundwater samples in the mid-continent with respect to the meteoric water line (MWL) of Craig (1961) and Taylor (1974). Symbols are identified in Fig. 2.1A. δD and $\delta^{18}O$ values are relative to SMOW (Standard Mean Ocean Water).

This lack of data close to the Colorado Front Range could be due to the fact that no wells have been drilled in that area due to the depth to the WIP strata.

Throughout the WIP in the mid-continent there exists a spatial correspondence between geochemistry and flow direction (Fig. 2.5). Musgrove and Banner (1993) observed at a smaller scale the same geochemical and spatial correspondence. On the larger scale, Group 2 does not exhibit the same geochemical and geographic correspondence as observed in a smaller scale (Fig. 2.1B and 2.5). This may be due to the fact that these groundwaters are not just the result of mixing but are also affected by water-rock interaction, much

more so than Groups 1 and 3. This interaction was not so extensive as to affect the stable isotopic signature of the groundwaters.

The regional extents of the groups suggest that there is hydraulic continuity on the scale of 1200 km in the Western Interior Plains aquifer system (Fig. 2.1A). The results from mixing models explain the heterogeneity and variability found in the different water types in the mid-continent (Fig. 2.3C). We can also see from those mixing models how those differences in water types can be explained by different degrees of mixing of the water types, with the areas where the groups come into contact exhibiting the highest degree of mixing.

If the WIP was not a hydraulically continuous flow system, then the three identified endmembers, i.e. Endmember 1, 2 and 3, would occur as discrete flow systems and not show evidence mixing with each other. However, within each groundwater group present in the WIP there is a transition from each endmember water to waters with geochemical and isotopic values that are intermediate between values of the two other endmembers present in the mid-continent.

Conclusions

The WIP exhibits a wide range of geochemical and isotopic variability that reflect a range of fluid mixing processes over a 1200 km scale. The identification of three groundwater groups through the quantification of groundwater mixing processes allows the constraint of possible flowpaths and models for the origin of these groundwaters. The systematic variations in the geochemical

concentrations and isotopic values of the WIP groundwaters and their regional extent over the mid-continent, suggest that the WIP is hydraulically continuous.

The characterization of the WIP can be used as a modern analog for ancient and modern continental-scale flow systems. The implications of continental-scale groundwater systems, such as the WIP, span across diverse processes, from carbon dioxide sequestration to MVT ore genesis. A more thorough

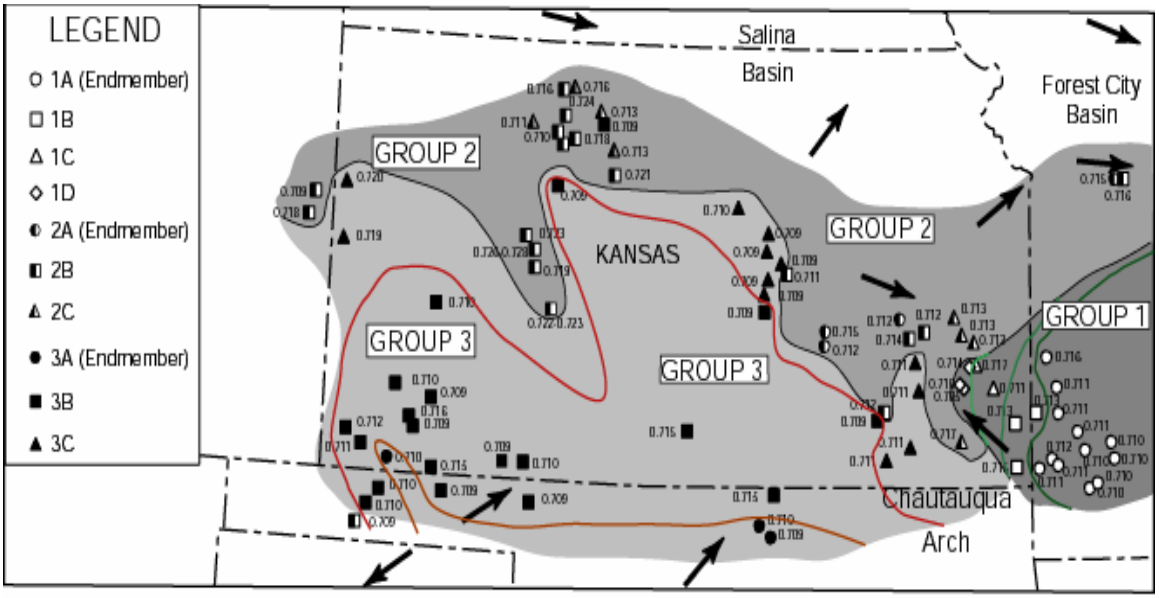


Fig. 2.5 Close up of the study area showing water compositional groups locations and their regional extent. Groundwaters were divided into groups according to their geochemical and isotopic character. Groups 1 and 3 have been countoured according to their intermediates. It can be observed that these two groups have the same geographical variability that was depicted,at a much smaller scale, by Musgrove and Banner, 1993. Arrows depict direction of flow. Groundwater flow direction based on Larson (1971), Jorgensen (1989), and Jorgensen et al. (1986).

understanding of this system will provide a better decision-making process regarding the disposal of hazardous materials and their possible leakage through the confining system into potable water sources.

References

Bachu, S., 1995, Synthesis and Model of Formation-Water Flow, Alberta Basin, Canada, AAPG Bulletin, Vol. 79, No. 8, pp. 1159-1178.

Bachu, S, Brulotte, M. Grobe, M, and Stewart, S., 2000, The sustainability of the Alberta subsurface for carbon dioxide sequestration in geological media, Earth Science Report, March 2000, 86 p.

Banner, J. L., Musgrove, M., and Capo, R. C., 1994, Tracing Ground-Water Evolution in a Limestone Aquifer Using Sr Isotopes: Effects on Multiple Sources of Dissolved Ions and Mineral-Solution Reactions, Geology, Vol. 22, pp. 687-690.

Banner, J. L., Wasserburg, G. J., Dobson, P. F., Carpenter, A. B., and Moore, C. H., 1989, Isotopic and Trace Element Constraints on the Origin and Evolution of Saline Groundwaters from Central Missouri, Geochimica and Cosmochimica Acta, Vol., 53, pp. 383-398.

Belitz, K., and Bredehoeft, J. D., 1988, Hydrodynamics of the Denver Basin: Explanation to Subnormal Fluid Pressures, AAPG, Vol. 72, No. 11, pp. 1334-1359.

Bentley, H. W., Phillips, F. M., Davis, S. N., Habermehl, M. A., Airey, P. L., Calf, G. E., Elmore, D., Gove, H. E., and Torgensen, T., 1986, Chlorine 36 Dating of Very Old Groundwater 1. The Great Artesian Basin, Australia, Water Resources Research, Vol. 22, No. 13, pp. 1991-2001.

Bethke, C. M. and Marshak, S., 1990, Brine Migrations across North America – The Plate Tectonics of Groundwater *in:* Wetherill, G. W., Albee, A. L. and Stehli, F. G., (eds.) Annual Review of Earth and Planetary Sciences, Vol. 18, pp. 287-315.

Broecker, W. S., and Denton, G. H., 1989, The Role of Ocean-Atmosphere Reorganizations in Global Cycles, Geochimica et Cosmochimica Acta, Vol. 53, pp. 2465-2501.

Bruant, R. G., Celia, M. A., Guswa, A. J., and Peters, C. A., 2002, Safe storage of CO_2 in deep saline aquifers, Environmental Science and Technology, Vol. 36, No. 11, pp. 240-245.

Burrus, R. C., and Hatch, J. R., 1989, Geochemistry of Oils and Hydrocarbon Source Rocks, Greater Anadarko Basin; Evidence For Multiple Sources of Oils and Long-Distance Oil Migrations, Oklahoma Geological Survey Circular, No. 90, pp. 53-64.

Calf, F. E. and Habermehl, M. A., 1983 Isotope Hydrology and Hydrochemistry of the Great Artesian Basin, Australia, *in*: Isotope Hydrology 1983, pp. 397-413, Int. At. Energy Agency, Vienna.

Cathles, L . M. III., 1990, Scales and effects of fluid flow in the upper crust, Science, Vol. 248, Issue No. 4953, pp. 323-329.

Chaudhuri, S., Broedel, V., and Clauer, N., 1987, Strontium Isotopic Evolution of Oil-Field Waters from Carbonate Reservoir Rocks in Bindley Field, Central Kansas, U.S.A., Geochimica et Cosmochimica Acta, Vol. 15, pp. 45-53.

Chaudhuri, S., Robinson, R., Clauer, N., and Jones, L. M., 1992, Evolution of Formation Waters in Early Pennsylvanian Morrowan Sandstones in the Hugoton Embayment of the Anadarko Basin, Southern Midcontinent, U.S.A., Oklahoma Geological Circular No. 93, pp. 160-174.

Clayton, R. N., Friedman, I., Graf, D. L., Mayeda, T. K., Meents, W. F., and Shimp, N. F., 1966, The Origin of Saline Formation Waters. 1. Isotopic Composition, J. Geophys. Res., Vol. 71, pp. 3869-3882

Craig, H., 1961, Isotopic Variations in Meteoric Waters, Science, Vol. 133, pp. 1702-1703.

Davis, S. N., Campbell, D. J., Bentley, H. W., and Flynn, T. J., 1985, Ground Water Tracers, National Water Well Association, Worthington, Ohio, 199 p.

Dansgaard, W., 1964, Stable isotopes in precipitation, Tellus, Vol. 16, pp. 436-468.

Dutton, A. R., 1994, Sources and ages of ground water in unconfined and confined aquifers beneath the U.S. high plains, Final technical report, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas.

Garven, G., 1985, The role of regional fluid flow in the genesis of the Pine Point Deposit, Western Canada sedimentary basin, Economic Geology and the Bulletin of Economic Geologists, Vol. 80, Issue 2, pp. 307-324.

Girard, P., Hillaire-Marcel, C., and Oga, M. S., 1997, Determining the Recharge Mode of Sahelian Aquifers Using Water Isotopes, Journal of Hydrology, Vol. 197, pp. 189-202.

Gunter, W. D., Perkins, E. H., and Hutcheon, I., 2000, Aquifer Disposal of Acid Gases: Modeling of Water-Rock Reactions for Trapping of Acid Wastes, Applied Geochemistry, Vol. 15, pp. 1085-1095.

Hitchon, B., and Friedman, I., 1969, Geochemistry and Origin of Formation Waters in the Western Canada Basin – I Stable Isotopes of Oxygen and Hydrogen, Geochimica et Cosmochimica Acta, Vol. 33, pp. 1321-1349.

Horita, J., Bencoe, J. G., and Cole, D. R., 2001, Fundamental geochemical research on long term carbon sequestration in subsurface, AAPG Expanded Abstracts, June 2001, pp. 92.

Jorgensen, D. G., 1989, Paleohydrology of the Anadarko Basin, Central United States, Oklahoma Geological Survey Circular No. 90, 176-193.

Jorgensen, D. G., Helgesen J. O., and Imes, J. L., 1993, Regional Aquifers in Kansas, Nebraska, and Parts of Arkansas, Colorado, Missouri, New Mexico, Oklahoma, South Dakota, Texas and Wyoming-Geohydrologic Framework, USGS Professional Paper 1414-B.

Jorgensen, D. G., Leonard, R. B., Signor, D. C., and Helgesen, J. O, 1986a, Midwest Regional Aquifer Study: Regional Aquifer System Analysis Program of the USGS, USGS Circular 1002, pp. 132-140.

Larson, T. G., 1971, Hydrodynamic Relationships in the Mid-Continent *in*: Cram, I. H. (ed) Future Petroleum Provinces of the Mid-Continent – Their Geology and Potential, AAPG Memoir 15, Vol. 2, pp. 1043-1046.

Lopes, T. J. and Hoffman, J. P., 1997, Geochemical Analyses of Ground-Water Ages, Recharge Rates, and Hydraulic Conductivity of the N Aquifer, Black Mesa Area, Arizona, USGS Water Resources Investigations Report 96-4190.

Mazor, E., 1991, Applied Chemical and Isotopic Groundwater Hydrology, Halsted Press, 274 p.

Mearns, E. W., and McBride, J. J., 1999, Hydrocarbon Filling History and Reservoir Continuity of Oil Fields Evaluated using $^{87}Sr/^{86}Sr$ Isotope Ratio Variations in Formation Water, with Examples from the North Sea, Petroleum Geoscience, Vol. 5, pp. 17-27.

Musgrove, M and Banner, J. L., 1993, Regional Ground-Water Mixing and the Origin of Saline Fluids: Midcontinent, United States, Science, Vol. 259, pp. 1877-1882.

Nicastro, L., 1983, Isotopic and chemical studies of oil-field waters associated with Upper Paleozoic rocks, Miner field, Ness County, Kansas, unpub. M.S., Kansas State University, 89 p.

Siegel, D. I., and Mandle, R. J., 1984, Isotopic Evidence for Glacial Meltwater Recharge to the Cambrian-Ordovician Aquifer, North-Central United States, Quaternary Research, Vol. 22, pp. 328-335.

Siegel, D. I., 1989, Geochemistry of the Cambrian-Ordovician Aquifer System in the Northern Midwest, United States, USGS Professional Paper 1405-D, 76 p.

Signor, D. C., 1988, Regional flow systems in the central United States, GSA Abstracts with Program 20, No. 2, p. 129.

Signor, D. C., and Imes, J. L., 1988, Geohydrology of Regional Aquifer Systems in Cretaceous and Older Rocks Underlying the Central U.S. *in:* Swain, L. A., and Johnson, I.A., Regional Aquifer Systems of the United States, Aquifers of the Midwestern Area, AWRA Monograph Series No. 13.

Solomon, D.K., Cook, P.G. and Sanford, W.E., 1998, Dissolved Gases in Subsurface Hydrology. In: C. Kendall and J.J. McDonnell (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, pp. 291-318.

Taylor, H. P., Jr., 1974, The Application of Oxygen and Hydrogen Isotope Studies to Problems of Hydrothermal Alteration and Ore Deposition, Econ. Geol., Vol. 69, pp. 843-883.

Torgensen, T., Habermehl, M. A., Phillips, F. M., Elmore, D., Kubik, P., Jones, B. G., Hemmick, T., and Gove, H. E., 1991, Chlorine 36 Dating of Very Old Groundwater 3. Further Studies in the Great Artesian Basin, Australia, Water Resources Research, Vol. 27, No. 12, pp. 3201-3213.

Tóth, J., 1995, Hydraulic Continuity in Large Sedimentary Basins, Hydrogeology Journal, Vol. 3, No. 4, pp. 4-16.

Webb, T., III, and Bryson, R. A., 1972, Late and Postglacial Climatic Change in the Northern Midwest, U.S.A.: Quaternary Estimated Derived from Fossil Pollen Spectra by Multivariate Statistical Analysis, Quaternary Research, Vol. 2, pp. 70-113.

Yapp, C. J., and Epstein, S., 1977, Climatic Implications of D/H Ratios of Meteoric Waters over North America (9,500-22,000 b.p.) as Inferred from Ancient Wood Cellulose C-H Hydrogen, Earth Planetary Science Letters, Vol. 34, pp. 330-350.

CHAPTER 3

THE ORIGIN AND EVOLUTION OF SALINE GROUNDWATER IN THE WESTERN INTERIOR PLAINS AQUIFER SYSTEM IN THE MID-CONTINENT, U.S.A.

Abstract

The Great Plains Aquifer System (GP) and the Western Interior Plains Aquifer System (WIP) in the mid-continent, USA, exhibit a wide range of chemical and isotopic variability that reflects a range of fluid mixing processes and two different mechanisms for the generation of saline fluids. The study area in the mid-continent extends 1200 km west to east, from the Colorado Front Range to Central Missouri and 500 km north to south from the Nebraska Panhandle to the Oklahoma Panhandle. Groundwater salinities range from 20,000 to 300,000 mg/l in the WIP and from 300 to 74,000 mg/l in the GP. Oxygen isotope values of groundwater range from -14‰ to 2.8‰ in the WIP and -13‰ to -10 ‰ in the GP. Hydrogen isotope values range from -100‰ to -5‰ in the WIP and from -101 ‰ to -81 ‰ in the GP. Strontium isotope values range from 0.70860 to 0.72476 in the WIP and from 0.70774 to 0.73189 in the GP. Analysis of the geochemical and isotopic data suggests that the salinity of Group 2 is the result of the dissolution of the Hutchison Salt Member of the Wellington Formation and evaporite deposits in the Nipewalla Group, while the salinity of Group 3 results from the evaporation of seawater. Elevated strontium isotope values suggest that some Group 2 samples have undergone a significant amount of water-rock interaction with Pennsylvanian shales, the Precambrian basement or argillaceous components within the rock.

Introduction

Saline groundwaters are an important part of the hydrologic cycle because they are the medium within, which oil and gas migrate. Therefore, understanding saline fluid migration is important in our management of these energy resources. There is also a public and regulatory concern over the use of deep basinal formations for disposal of hazardous waste and the associated potential of cross-formational flow to water supply aquifers (Wilson and Long, 1993). These concerns underscore the need to understand the origin and migration paths of saline brines so we can manage and determine disposal sites more effectively. Additionally, saline groundwaters play an important role in diagenetic processes such as dolomitization and precipitation of ore minerals (Bethke and Marshak, 1990).

Even though saline waters are ubiquitous in nearly every sedimentary basin, their origin is still a controversial subject (Hanor, 1987; Walter et al., 1990; Kloppmann et al., 2001). Three generalized processes have been invoked to account for the origin of salinity: 1) shale membrane filtration, 2) dissolution of evaporites, and 3) evaporation of seawater (Hanor, 1987). It is difficult to recognize , which processes produced the salinity since mixing with other groundwaters and water-rock interaction may alter the chemical character of brines.

Shale membrane filtration, which is driven by pressure resulting from the compaction of the sediments, results in the preferential passage of uncharged species and small and univalent cations relative to large divalent cations

(Bredehoeft et al, 1963). This process remains to be documented on a large scale and sufficient geochemical evidence exists with respect to the expected brine composition from other studies, therefore this process will not be considered when evaluating the origin of the saline fluids in the WIP (Hanor, 1983; Land and MacPherson, 1992). Based on studies of Gulf Coast saline Ca-Cl groundwaters by Land and Macpherson (1992) and Land (1995), shale membrane filtration can not explain: 1) the increase in Ca groundwaters resulting from filtration. It also fails to explain the increase of other large divalent ions such as Sr and Ba and the decrease concentrations of Mg, 2) univalent ions are well correlated with one another irrespective of Ca concentrations, 3) Br/Cl ratios do not increase with increasing salinity (i.e., filtration), 4) Rb/Li ratios are nearly constant at different salinities. Similar trends in the geochemical character of Group 3 groundwater lead to the same inferences regarding shale membrane filtration for the WIP.

Geochemical data, in particular bromide, chloride and sodium, together with H, O and Sr isotopes from WIP groundwater will be used to investigate the origin of the salinity and the extent to which those fluids have been altered by water-rock interaction. In Chapter 2, I identified three geochemical endmembers of distinct origin in the WIP of southwest Kansas, southeast Missouri, and northeast Oklahoma: Endmember 1, a dilute groundwater recharged in the Ozark Plateau; Endmember 2, a saline groundwater possibly originating in the Colorado Front Range; and Endmember 3, the most saline endmember, originating in the Anadarko Basin (Musgrove and Banner, 1993). Groundwaters from this study

together with data from previous studies (Musgrove and Banner, 1993; Chaudhuri et al., 1987, 1992; Nicastro, 1983; and Banner et al., 1989) are used to investigate processes of water:rock interaction, mechanisms for the generation of salinity, and the processes that altered the geochemical and isotopic character of the waters (Fig. 3.1). In Chapter 2 it was established that the geographical distribution of the three groups suggested that the WIP was hydraulically continuous. Based on that idea, this chapter will attempt to explain the origin and evolution of the groundwater in the WIP, in particular with respect to Group 2 and Group 3.

Previous work

Musgrove and Banner (1993) identified three geochemical endmembers in the WIP in southwest Missouri, northeast Oklahoma, and southeast Kansas (Table 3.1). Endmember 1, originating in the Ozark Plateau of southwestern Missouri, is characterized as a dilute groundwater. Endmember 2, which originates to the west of their study area, is characterized as a Na-Ca-Cl saline groundwater. Finally, Endmember 3 groundwater is also a Na-Ca-Cl type but with higher total dissolved solids and higher stable H and O isotopic values than Endmember 2. Musgrove and Banner (1993) concluded that Endmember 2 groundwater acquired its salinity from the dissolution of Permian evaporites by meteoric water and its chemical character was subsequently altered through water-rock interaction and mixing with Endmembers 1 and 3 groundwaters. These authors propose that the salinity of Endmember 3 groundwater is due to

the evaporation of seawater. Water:rock interaction and mixing with Endmember 1 and 2 groundwaters gives Endmember 3 groundwater its present chemical character.

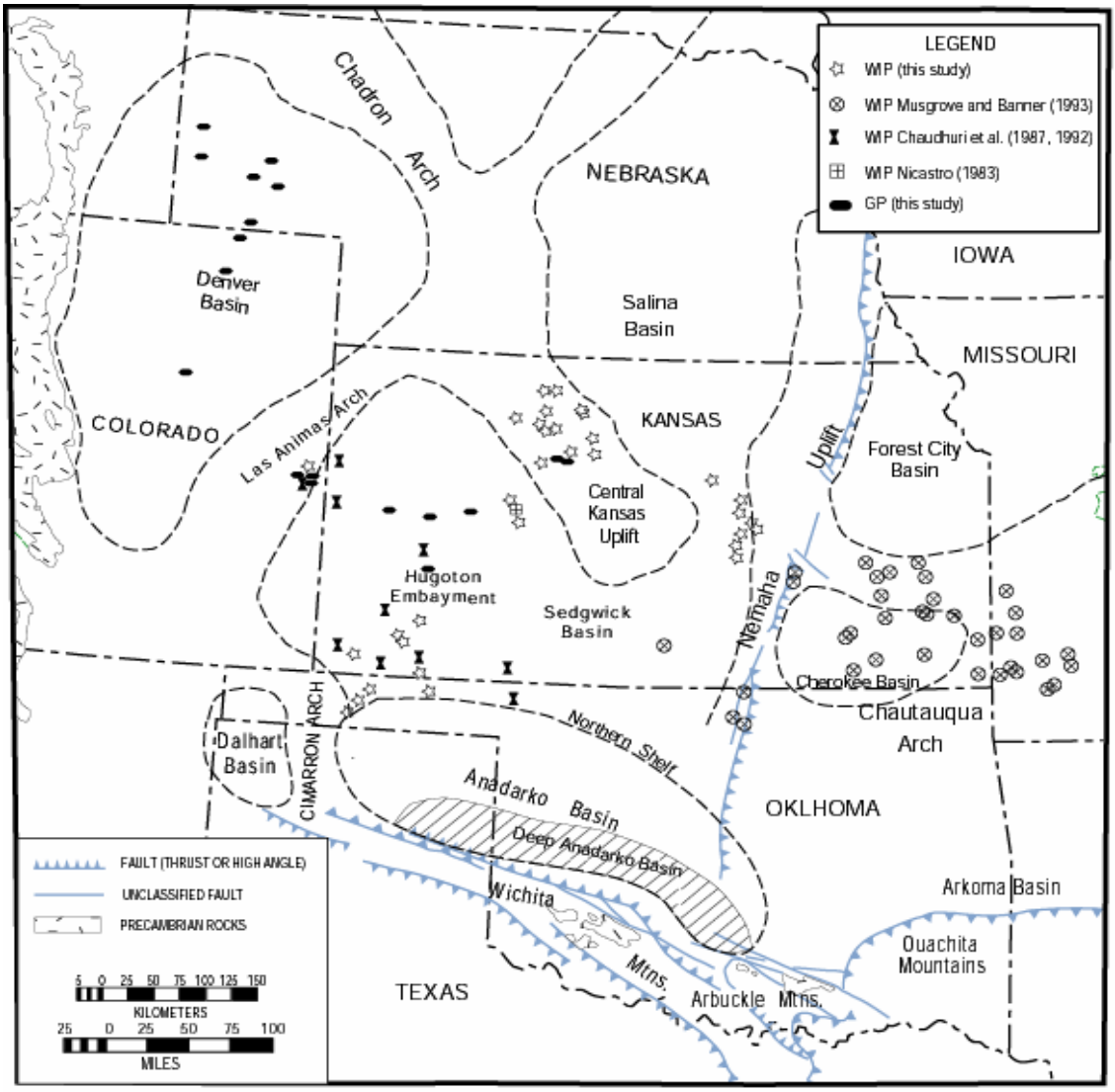


Fig. 3.1 Location of groundwater samples with respect to the structural features in the mid-continent. Groundwater samples were obtained from water and oil/gas wells. In southwestern Missouri samples were obtained from water wells. The remainder of the WIP groundwater was obtained from oil/gas wells. The GP groundwater in Kansas and in Banner county, Nebraska was obtained from water wells. The rest of the gP groundwater was collected from oil/gas wells. Modified from Larson (1971).

Table 3.1 Geochemical and isotopic ranges for groundwater from the WIP

Group	TDS mg/l	Temp (C)	pH	δ18O (per mil)	δD (per mil)	Cl (mg/l)	Br (mg/l)	SO4 (mg/l)	Na (mg/l)	Ca (mg/l)	Mg (mg/l)	Sr (mg/l)
1A	200 to 800	17 to 21	7.27 to 8.05	-6.8 to 5.4	-44 to -36	1.5 to 25	< 1	3.0 to 65	<1.02 to 19	8 to 100	5 to 22.0	0.04 to 0.4
1B	609 to 700	20.5 to 22.2	7.31 to 7.64	-6.5 to -6.7	-42 to -43	44 to 64	<1	10 to 61	66 to 140	31 to 63	16 to 29	0.6 to 1.4
1C	1320 to 3469	19.8 to 21.7	7.30 to 7.70	-6.3 to -6.70	-39 to -44	540 to 1680	2.5 to 3	2 to 170	300 to 1200	19 to 77	10 to 29	0.03 to 2.0
1D	6700 to 14100	18.7 to 27.8	7.06 to 7.71	-6.10 to -6.50	-39 to -42	3550 to 8000	14 to 29	0.6 to 350	2300 to 5200	100 to 300	59 to 150	5 to 16
2A	22200 to 34600	27.2 to 42.3	6.70 to 6.86	-12.4 to -14	-98 to -100	12100 to 19300	17 to 54	54 to 2100	7100 to 11000	800 to 1800	300 to 500	44 to 59
2B	42900 to 63200	20.9 to 28	5.80 to 6.68	-8.9 to -10.70	-70 to -84	26800 to 38200	46 to 75	1 to 1800	15000 to 20700	1600 to 3400	700 to 800	83 to 103
2C	9400 to 25300	16 to 30.9	6.90 to 7.39	-6.8 to -7.8	-50 to -60	5200 to 15000	12 to 28	3 to 100	3300 to 8600	170 to 900	93 to 300	10 to 30.4
3A	228700 to 249000	32.5 to 40.3	5.84 to 6.12	2.4 to 2.8	-5 to -6	169600 to 184200	360 to 620	12 to 150	77800 to 78300	16100 to 25900	2400 to 2800	800 to 1500
3B	113500 to 138000	30.3 to 51.6	6.32 to 6.71	-2.4 to -3.7	-32 to -42	73100 to 92400	150 to 350	160 to 600	41300 to 46400	5400 to 8900	1200 to 2900	200 to 1000
3C	62300 to 79200	24.4 to 30.1	6.45 to 7.25	-6.0 to -6.5	-58 to -50	38800 to 51200	120 to 150	3 to 8	22200 to 27500	2300 to 2900	750 to 1100	100 to 200

Groundwaters are from southwest Missouri, southeast Kansas, and northeast Oklahoma. The group classification is discussed within the text. Hydrogen and oxygen stable isotopes are relative to SMOW. This table includes data from Musgrove and Banner (1993), Musgrove (1993), Chaudhuri et al 1987, Chaudhuri et al., 1992, and Nicastro (1993). Group 1, 2 and 3 data is from Musgrove and Banner (1993) and Musgrove (1993), Group 2 and 3 data is from Chaudhuri et al, (1987, 1992), Nicastro (1983) and from this study.

Musgrove and Banner (1993) concluded that there are systematic spatial variations of major ion concentrations, stable isotope ratios, and geographic distribution of these three groups. In Chapter 2, it was demonstrated that the same groups were found over a 1200 km scale. I concluded in Chapter 2 that the same endmember spatial variations of major ion concentrations, stable isotope ratios and geographic distribution can be found across the mid-continent, supporting the idea that there is hydraulic continuity over a 1200 km scale. This study attempts to test the theories presented in the Musgrove and Banner (1993) study at a much larger scale and in a more complex system.

Chaudhuri et al. (1987) studied oil-field brines in the Mississippian Morrowan formation in south central Kansas. The oil-field waters were found to be Na-Cl type with an average salinity of 42,000 mg/l. The strontium isotopic signature of groundwaters in southwest Kansas ranged between 0.7221 to 0.7230, while the host carbonate rocks exhibit a strontium isotope signature ranging between 0.7090 and 0.7093. The results of these studies support the idea that the high strontium isotope signature is due to the interaction of groundwaters with alkali feldspars within the Precambrian crystalline rocks (Chaudhuri et al., 1987 and Nicastro, 1983). They also concluded that dissolution of evaporitic minerals, dolomitization, albitization of K-feldspar, and ion exchange with shales have altered the groundwaters.

Chaudhuri et al. (1992) studied the evolution of groundwaters from Early Pennsylvanian formations in the Hugoton Embayment of the Anadarko Basin. The salinity of these groundwaters in Pennsylvanian-aged rocks ranges from 52,000 to 244,500 mg/l TDS. Based on oxygen and hydrogen isotopic data, it was concluded by the authors that the Na-Cl brines mixed with a fresh groundwater, most likely originating at high elevations on the Colorado Front Range. Chaudhuri et al. (1992) further concluded that the salinity of the groundwaters originated from the evaporation of seawater or from diagenetically evolved water of unknown origin. Due to the limited extent of the study area, these authors were not able to denote the different groundwater endmembers in the WIP.

Dutton and Bein (1993) studied the origin of the salinity in the Palo Duro and Midland basins in Texas and the Anadarko basin in Oklahoma. Anadarko Basin groundwaters are Na-Ca-Cl brines, with total dissolved solids of more than 100,000 mg/l. The salinity in the groundwaters in the Anadarko Basin is proposed to be derived from Permian seawater in a halite precipitating lagoon (Dutton and Bein, 1993). This groundwater was intermittently mixed with fresh groundwater and modified by water:rock interaction.

Hydrogeologic Setting

The GP and the WIP lie within the presently tectonically stable interior of the North American craton. Variations in the present day depth to the top of the Precambrian basement show the effects of the Late Cretaceous-Early Tertiary Laramide orogeny that affected rocks ranging from Paleozoic to Early Tertiary.

The GP, also known as the Dakota aquifer, overlies the WIP aquifer system and confining system. The GP is composed predominantly of Cretaceous sandstones and shales (Fig. 3.2). In general, groundwater flow in the GP is from west-southwest to east-northeast with estimated average velocities ranging between 3×10^{-3} m/y to 3 m/y (Helgesen et al., 1993). Recharge to this aquifer system occurs in southeast Colorado and northeast New Mexico. Discharge occurs through springs in the Upper Cretaceous in the Nebraska panhandle, to the Arkansas River in central Kansas, and through oil, municipal, and irrigation wells (Dutton, 1994).

The WIP covers most of the mid-continent. This regional aquifer system is overlain by the Western Interior Plains confining system and underlain by the crystalline Precambrian basement. The WIP consists of rocks of Cambrian through Lower Pennsylvanian age (Signor and Imes, 1988) that include dolomites, limestones, sandstones, and shales (Fig. 3.2). A detailed cross section of the mid-continent can be found in Appendix D. The thickness of the WIP, including the Western Interior Plains confining system ranges between less than 152 m to more than 914 m (Miller and Appel, 1997).

The WIP is absent or thin on structural highs, such as the Nemaha uplift, and is thick in basins, such as the northern flank of the Anadarko Basin. Groundwater within this aquifer system moves regionally very slowly from west to east due the low intrinsic permeability and the minimal hydraulic gradient of the area (Jorgensen et al., 1993).

Estimated values of regional intrinsic permeability range from 10^{-12} ft^2 ($9.3x10^{-13}$ m^2) in eastern Kansas to 10^{-16} ft^2 ($9.3x10^{-17}$ m^2) in southwestern Oklahoma and 10^{-18} ft^2 ($9.3x10^{-19}$ m^2) in eastern Colorado (Signor and Imes, 1988). Discharge from the WIP occurs through natural springs in the Cambrian-Ordovician and Mississippian limestones in central and southern Missouri, to the Missouri and Mississippi rivers, and through oil and supply wells in Kansas, southwest Missouri, eastern Colorado, and northern Oklahoma.

Geohydrologic unit		Important stratigraphic units	Time-stratigraphic unit
High Plains aquifer		Ogallala Formation and unconsolidated deposits	Quaternaryand Tertiary
Great Plains confining system		Pierre Shale, Niobrara Formation, and Carlile Shale	Upper Cretaceous
Great Plains aquifer system	Maha aquifer	Dakota Sandstone, "D" sandstone, and "J" sandstone	Lower Cretaceous
	Apishapa confining unit	Kiowa Shale and equivalent of Skull Creek Shale	
	Apishapa aquifer	Cheyenne Sandstone	
Western Interior Plains confining system		Morrison Formation, Nipewalla Group, Lansing Group, Kansas City Group, Wellington Formation, Entrada Sandstone	Jurassic through Upper Mississippian (Chesterian)
Western Interior Plains aquifer system	Upper unit	Meramecian, Osagean,andKinderhookian rocks	Upper Mississippian through Upper Cambrian
	Confining unit	Chattanooga and Woodford Shales	
	Lower unit	Hunton Group, Viola Limestone, Arbuckle Group, and Reagan Group	
Basement confining unit		Mostly igneous and metamorphic rocks	Cambrian and Precambrian

Fig. 3.2 Geohydrologic column of the study area (modified from Jorgensen et al., 1993).

Results

Groundwater samples from oil and gas wells, in Kansas, eastern Colorado, and the Oklahoma Panhandle were collected during August 1996 and October 1998 from Cambrian to Lower Pennsylvanian units, ranging in depth from 795 m to 2,042 m. Sampling and analytical techniques are described in

Appendix A, full geochemical and isotopic data for all the groundwaters collected in this study is in Appendix B, and stiff diagrams for all the groundwaters collected in this study are provided are Appendix C.

The results of analyses for major element concentrations, temperature, pH, and hydrogen, oxygen, and strontium isotopes for central and western Kansas, eastern Colorado, and the Oklahoma panhandle are presented in Tables 3.2 and 3.3. Groundwaters from the WIP exhibit a wide range of elemental and isotopic compositions. The range of salinity in the WIP is extreme, ranging from 200 to 249,000 mg/l. The isotopic composition of the groundwater in the WIP ranges from -14‰ to 2.8‰ and -100‰ to -5‰ for $\delta^{18}O$ and δD, respectively (Table 3.1). Strontium isotope values range from 0.70860 to 0.72476 (Table 3.2). The predominant constituents in WIP groundwater are Na, Cl, Ca, and SO_4. Figure 3.3 has stiff diagrams for representative water samples from Groups 2 and Group 3. It can be observed that in general the WIP groundwaters are Na-Ca-Cl waters.

Groundwaters from this study together with groundwaters from Chaudhuri et al. (1987, 1992) and Nicastro (1983) are classified into geochemical and isotopic groups using the same criteria as Musgrove and Banner (1993; Tables 3.2 and 3.3). This study will use data from all of these studies to investigate the origin and evolution of the groundwaters in the WIP.

Table 3.2 Mid-Continent groundwater - Geochemical and isotopic analyses

Well name	Group	TDS mg/l	Temp (C)	pH	$^{87}Sr/^{86}Sr$	δ18O (per mil)	δD (per mil)
Cooley #1	2B	20,000	35.20	6.53	0.71821	-10	-77.11
Cooley #4	2B	45,500	35.60	6.70	0.71026	-8.3	-76.10
Fernback J #1	2B	27,000	22.3	7.33	0.70909	-9.1	-62
Groening # 1	2B	45,400	27.0	6.87	0.71114	-11	-89
Miller #4	2B	36,000	27.90	6.40	-	-8.5	-73.50
Shear "A"	2B	30,300	33.30	6.65	0.72476	-10	-79.20
UPRC 1-35	2B	35,800	38.80	7.89	0.70898	-7.2	-83.00
Von Lintel #2	2B	50,400	34.50	6.36	0.72095	-8.7	-77.30
Wiltrout #1	2B	62,000	31.60	7.04	0.71586	-4.5	-59.50
Schmalzried	2C	50,000	22.1	6.51	0.71860	-8.3	-65.4
George West	2C	66,500	21.1	6.31	0.71303	-8	-69.1
Holley #201	2C	63,700	29.20	6.80	0.71095	-7.3	-66.80
Ray "A" #4	2C	58,900	28.90	6.78	0.71571	-4.4	-56.50
Kriley E2	2C	64,400	25.2	6.73	0.71329	-6.2	-66.7
Warren #1	2C	64,800	35.00	7.00	0.72372	-4.5	-54.00
Van Meter # 1	3B	94,000	24.2	6.78	0.70902	-4.1	-45.9
Hart # 1 LSE	3B	85,000	23.2	6.50	0.70929	-4.1	-44.9
Kulhmeier #1	3B	89,000	20.4	7.04	0.70922	-3.6	-42.3
Morrison #1	3B	95,200	25.1	6.70	0.71009	-7	-64.3
Orland Unrue #2	3B	91,000	20.8	7.07	0.70945	-5.3	-55.6
Roland Ratzloff #1	3B	84,000	17.6	6.80	0.70923	-3.5	-41.6
Boles F - 1	3C	160,200	22.8	6.48	0.71549	-2.8	-34.1
Charles 1-12	3C	186,000	22.0	6.56	0.70872	0.8	-26.1
Franze E-1	3C	217,000	25.2	6.51	0.70897	0.8	-24.9
Hanke A-1	3C	190,000	23.5	6.52	0.70924	0.5	-21.1
James O'Dea A-1	3C	128,500	18.0	6.65	0.71629	-3.5	-36
Kriley G2	3C	136,000	18.2	6.85	0.70879	-3	-45.4
Mowrey W.H. #1	3C	246,600	22.7	6.96	0.71002	-0.7	-27.4
Rathjen #1	3C	238,800	22.9	6.92	0.71069	-2	-29.3
Regier # 1 (A)	3C	188,300	25.3	6.05	0.70860	1.4	-16.7
Straily	3C	176,100	27.80	6.60	0.70898	-0.3	-36.90
USA No. AD-2	3C	181,500	22.8	6.14	0.71146	0.7	-18.3
GP1		5,700-376	40.1-22.5	8.50-7.20	0.7098-0.70774	-12.7 to -7.8	-100 to -52
GP2		129,800-8,900	39-30	8.10-6.7	0.73189-0.70814	-11.5 to -4.60	-89.2 to -4.60
Seawater		36000	25	7.89		0	0

Range of geochemical and isotopic parameters for central-west Kansas, eastern Colorado, the Oklahoma Panhandle, and the Nebraska Panhandle. Group classification is discussed in the text. Analytical methods and sample information collection is also provided in Appendix A. Seawater data is from Faure (1986). δD and δ^{18}O values are relative to SMOW.

Table 3.3 Mid-Continent groundwater - Geochemical analyses

Well name	Group	Cl (mg/l)	Br (mg/l)	SO4 (mg/l)	Na (mg/l)	Ca (mg/l)	Mg (mg/l)	Sr (mg/l)	K/Rb
Cooley #1	2B	9,000	8	1,800	6,500	450	380	20	
Cooley #4	2B	24,500	50	1,800	15,700	2,200	560	60	
Fernback J #1	2B	12,200	60	5,000	9,000	350	210	7	884
Groening # 1	2B	26,600	100	1,800	14,200	1,800	580	80	901
Miller #4	2B	19,900	40	1,900	10,900	1,700	530	55	
Shear "A"	2B	15,800	20	2,000	9,900	1,500	400	45	
UPRC 1-35	2B	15,100	6	4,000	12,100	330	220	14	
Von Lintel #2	2B	26,900	50	2,200	17,300	2,600	620	65	
Wiltrout #1	2B	34,000	40	2,200	22,600	2,100	460	59	
Schmalzried	2C	29,400	100	3,000	14,100	2,100	600	60	355
George West	2C	39,500	100	1,500	20,700	2,600	890	140	
Holley #201	2C	34,900	10	700	25,700	650	340	60	
Ray "A" #4	2C	31,700	25	1,900	21,900	2,000	450	60	
Kriley E2	2C	39,100	110	2,800	19,300	2,100	570	70	700
Warren #1	2C	35,500	30	1,900	24,100	2,400	470	70	
Van Meter # 1	3B	60,200	170	900	27,900	3,300	1,200	280	962
Hart # 1 LSE	3B	53,400	170	180	26,800	3,000	1,000	240	867
Kulhmeier #1	3B	56,200	170	140	28,600	2,700	830	220	794
Morrison #1	3B	61,100	180	1,300	27,400	3,800	1,100	140	835
Orland Unrue #2	3B	55,600	200	1,400	28,500	3,800	1,000	230	895
Roland Ratzloff #1	3B	54,800	150	140	25,700	2,200	680	170	911
Boles F - 1	3C	100,300	350	1,100	47,600	8,500	1,700	310	451
Charles 1-12	3C	117,500	430	600	54,100	10,300	2,400	480	906
Franze E-1	3C	137,000	470	740	67,300	8,600	2,100	415	874
Hanke A-1	3C	119,500	438	600	55,800	10,800	2,200	550	752
James O'Dea A-1	3C	80,600	270	800	36,400	8,200	1,600	300	541
Kriley G2	3C	89,300	240	200	38,600	5,200	1,900	280	983
Mowrey W.H. #1	3C	155,600	540	2,500	79,500	6,500	1,800	150	1197
Rathjen #1	3C	149,300	450	2,600	81,400	3,700	1,300	80	1216
Regier # 1 (A)	3C	117,000	450	400	56,100	9,900	3,000	1,700	608
Straily	3C	102,300	45	1,700	65,100	4,700	1,300	160	
USA No. AD-2	3C	113,000	400	400	49,800	14,600	2,200	1,300	390
GP1		930-7	6.3-0.03	284-10	970-43	156-7	13.5-0.005	3.4-0.12	
GP2		73,600-12,300	27-6.6	3,300-400	50,300-4,000	1,800-3.3	395-0.7	78.1-1	
Seawater		19800	69	2770	11030	425	1310	8.3	

Range of geochemical and isotopic parameters for central-west Kansas, eastern Colorado, the Oklahoma Panhandle, and the Nebraska Panhandle. Group classification is discussed in the text. Analytical methods and sample information collection is also provided in Appendix A. Seawater data is from Faure (1986)

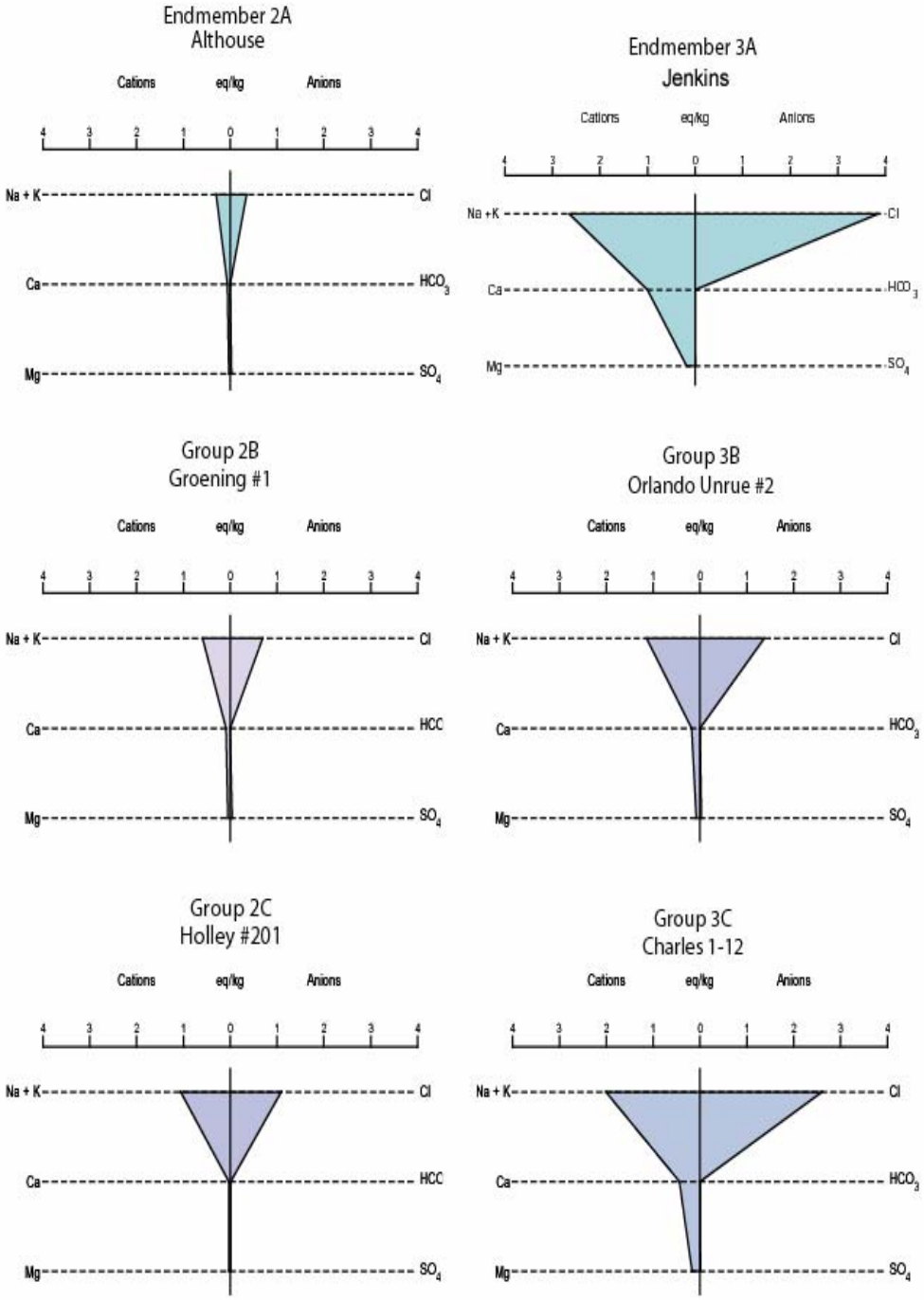


Fig. 3.3 Stiff diagrams of representative groundwater samples from Groups 2 and 3. Both groups are Na-Cl groundwaters. It can be observed that Group 3 groundwaters have higher total dissolved solids. Stiff diagrams were constructed in the Geochemist's Workbench (Bethke, 1994).

In the study area Groups 2B, 2C, 3B and 3C groundwaters were found (Fig. 2.5, chapter 2). A summary of their geochemical and isotopic parameters is provided in Tables 3.2 and 3.3. No endmembers of Group 2 and 3 as defined by Musgrove and Banner (1993), i.e. Group 2A and Group 3A, were found in the study area.

Group 2 Groundwater

Group 2B groundwaters occur mainly in central Kansas and eastern Colorado, and have salinities ranging from 20,000 to 62,000 mg/l TDS, with Cl ranging from 9,000 mg/l to 34,000 mg/l and Na ranging from 6,500 to 22,600 mg/l. Strontium isotope values range from 0.70889 to 0.72476. Group 2B waters have $\delta^{18}O$ and δD values that range from -11‰ to -4.5‰ and -83‰ to -59‰, respectively (Tables 3.1, 3.2 and 3.3). The groundwaters from Group 2 are classified as Na-Ca-Cl waters (Fig. 3.3)

Group 2C occurs mainly in central Kansas and the Oklahoma panhandle, and has salinities ranging from 58,900 to 66,500 mg/l TDS, with Cl concentrations ranging from 31,700 to 39, 5000 mg/l, and Na concentrations ranging between 19,300 to 25,700 mg/l (Tables 3.1, 3.2 and 3.3). Strontium isotope values range from 0.71303 to 0.72372. O and H isotope delta values range between -8 ‰ to -4 ‰ and -69 ‰ and -54‰, respectively. Groundwaters from Group 2C are also classified as Na-Ca-Cl waters (Fig. 3.3)

Group 3 Groundwater

Group 3B occurs in central Kansas and has salinities of 160,200 to 246,600 mg/l, with Cl concentrations of 100,300 to 155,600 mg/l and Na of 36,400 to 81,400 mg/l (Tables 3.1, 3.2, and 3.3). Strontium isotope values range from 0.70902 to 0.71009. Oxygen isotope delta values range from -7‰ to –3.5‰ and hydrogen isotope delta values range from -64.3‰ to -41.6‰. These groundwaters are classified as Na-Ca-Cl waters (Fig. 3.3)

Group 3C waters occur in central and southwest Kansas and the Oklahoma panhandle. Groundwaters in this group have TDS concentrations that range from 84,000 to 95,200 mg/l. The concentration of chloride ranges between 53,400 to 61,100 mg/l while the concentration of Na ranges between 25,700 to 28,600 mg/l (Tables 3.1, 3.2, and 3.3). Strontium isotope values for this group range from 0.70860 to 0.71629. Oxygen isotope delta values range from -3.5‰ to 1.4‰ and H isotope delta values range from -45 ‰ to -16‰. This water has been classified as Na-Ca-Cl groundwater (Fig. 3.3). Additionally, groundwater samples 2B, 2C, 3B, and 3C in central-west-southwest Kansas, eastern Colorado, and northwest Oklahoma are generally enriched relative to seawater in Sr, Mg, Ca, and SO_4.

Great Plains (GP) aquifer groundwater

The GP endmember is the average composition of groundwater collected in central western Kansas, eastern and northeast Colorado, and the Nebraska panhandle in this study and samples studied by Dutton (1994). The GP consists

mainly of Cretaceous sandstones and shales that are overlain by the Great Plains confining system and underlain by shales and evaporites of the Western Interior Plains confining system (Fig. 3.2)

The groundwaters can be divided into two distinct groups according to their chemical and isotopic values, GP1 and GP2. GP1 groundwater, present mainly in western Kansas, has a TDS ranging from 370 to 5700 mg/l. The concentration of chloride in the GP1 ranges between 6 to 930 mg/l, sodium ranges between 43 to 970 mg/l and bicarbonate ranges between 180 to 2300 mg/l. The isotopic composition of GP1 ranges between -12.‰ to -8‰ and -100‰ to -52‰ for $\delta^{18}O$ and δD, respectively. The GP2 groundwater has TDS ranging from 8,900 to 129,800 mg/l. The isotopic composition of GP2, present in eastern Colorado and the Nebraska panhandle, ranges from -12‰ to -5‰, and -89‰ to -55‰ for $\delta^{18}O$ and δD, respectively. Chloride concentrations range from 12,300 to 73,600 mg/l, while Na ranges from 4,000 to 50,300 mg/l. The GP1 Group is Na-HCO_3-Cl type water, while the GP2 Group is a Na-Cl water type. An in depth discussion of the GP is provided in Chapter 4.

Br-Cl variations

Bromide and chloride concentrations have been used to provide clues as to the origin of the salinity in groundwater. The concentrations of these constituents are plotted together with the seawater evaporation trend from McCaffrey et al. (1987) and the Permian halite dissolution trend from Gogel (1981) (Fig. 3.4). For groundwaters that acquired their salinity by halite

dissolution, Na/Br and Cl/Br will be strongly increased over that of seawater. The Na/Br ratio for modern seawater is 162, for a halite dissolution brine this ratio ranges from 400 to 5800 (Gogel, 1981), and for evaporated seawater this ratio ranges from 0.62 to 162 (Carpenter, 1978). Group 2 water has Na/Br ratios ranging form 144 to 2521, while Group 3 has Na/Br ratios ranging from 126 to 1445. The range in values for the Cl/Br ratios for Group 2 is 210 to 3420 and for Group 3 this range is between 280 and 2270.

Groups 2B and 2C plot on the trend calculated for the dilution of halite dissolution brines and along the halite dissolution trend (Figs. 3.4 and 3.5). This supports the idea that their salinity originated from the dissolution of Permian halite (Gogel, 1981) (Figs. 3.4 and 3.5). Groups 3B and 3C plot along the seawater evaporation trend with concentrations of Br and Cl higher than those of modern seawater (Fig. 3.4), while they plot along the seawater evaporation trend in the Na/Br-Cl/Br plot (Fig. 3.5).

Mineral-solution saturation variations

Saturation indices were calculated using NETPATH (Plummer et al., 1991). Most of Group 1 and 2 groundwaters are oversaturated with respect to calcite and undersaturated with respect gypsum (Fig. 3.6). Endmember 3A and

Group 3C are oversaturated with respect to calcite and undersaturated with

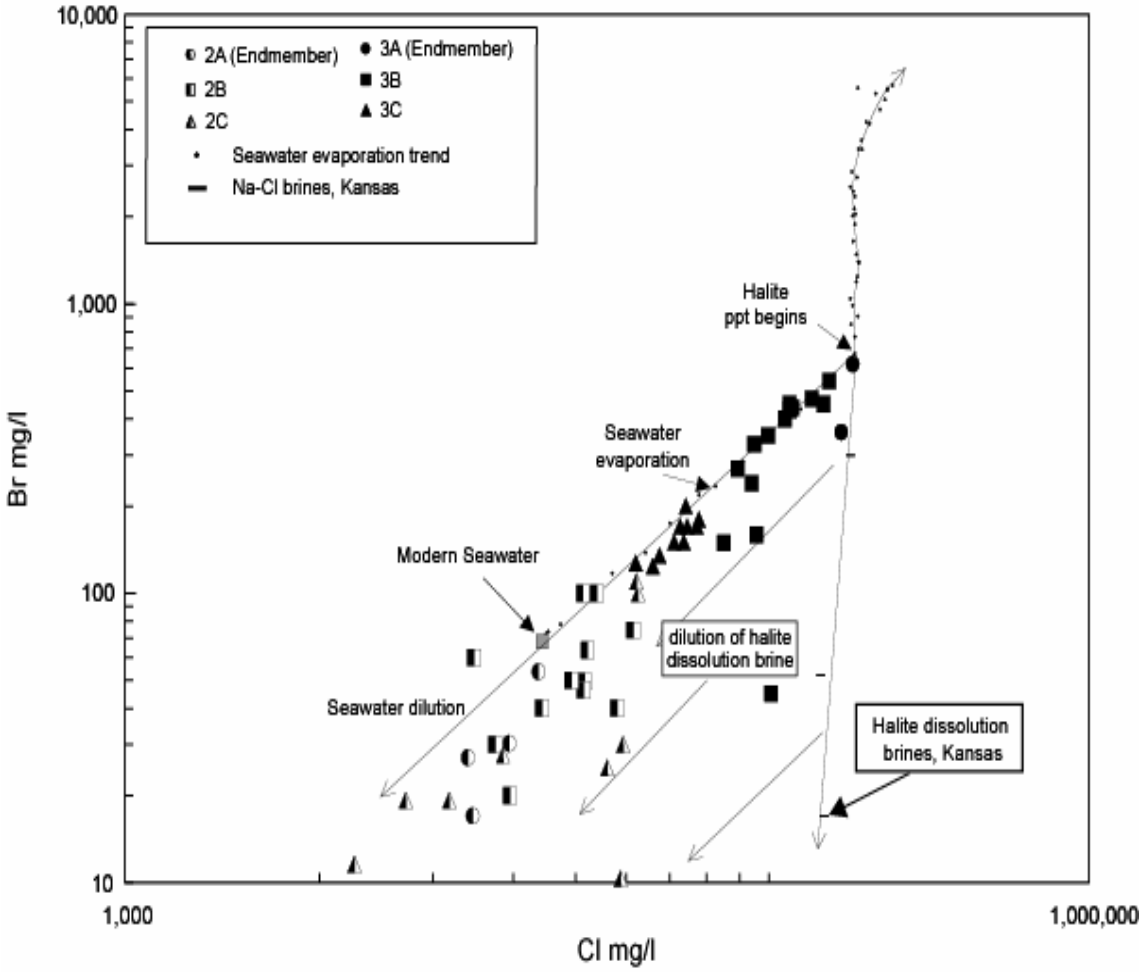


Fig. 3.4. Br-Cl variations for WIP groundwaters from the mid-continent. Samples for Chaudhuri (1987, 1992) and Nicastro (1983) were not plotted due to lack of Br data. Seawater evaporation trend is from McCaffrey et al (1987), halite dissolution trend for central Kansas is from Gogel (1981). Most of Group 3 groundwaters fall along the seawater evaporation trend just short of the onset of halite precipitation while most of Group 2 groundwaters fall within the dilution of halite dissolution brines field.

respect to gypsum. Some Group 3B groundwaters however, are oversaturated with respect to calcite while others are undersaturated with respect to calcite. Some of Group 3B groundwater is oversaturated with respect to gypsum (Fig

3.6). All of the samples are oversaturated with respect to quartz except three (Fig. 3.6).

Oversaturation with respect to quartz may indicate interaction with silicates. Group 3 exhibits the highest oversaturation with respect to quartz while Group 1 exhibits the lowest oversaturation with respect to quartz. Interaction with Pennsylvanian shales could provide the excess quartz in solution (Fig. 3.6). Additionally, Pennsylvanian shales also contain minor interbedded sandstone units that could provide an additional source of silicate (Franz, 1985; Robinson et al, 1985).

O and H Isotopes

Oxygen and hydrogen isotopic compositions of the groundwaters from this study and water sampled in previous studies (Musgrove and Banner, 1993, Chaudhuri, 1987, 1992, and Nicastro, 1983) are compared to the Global Meteoric Water Line (Fig. 2.4, Chapter 2). Endmember 1 plots on the Meteoric Water Line. Group 2 groundwaters plot to the right of the Meteoric Water line, this could be the result of water:rock interaction or mixing with other groundwater. Group 3 groundwaters plot to the right of the Meteoric Water Line and exhibit a trend of increasing H and O isotope values with increasing salinity (Fig. 2.4, Chapter 2). A more in depth analysis of H and O isotope values for the WIP groundwaters is provided in Chapter 2.

Strontium isotopes

Strontium isotopic values of the WIP groundwater range widely from 0.70872 to 0.72476 (Fig. 2.5 Chapter 2, Table 3.2). Group 2 exhibits the most radiogenic signatures with values of 0.70889 and 0.72476. Strontium concentrations for Group 2 are intermediate between the Group 1 and Group 3 (Tables 3.1 and 3.2), ranging between 7 and 140 mg/l. Studies of oilfield brines commonly find elevated $^{87}Sr/^{86}Sr$ values relative to the strontium isotopic value for seawater for the corresponding age of the host hydrostratigraphic unit (Chaudhuri et al., 1987; Chaudhuri et al., 1992, Sunwall and Pushkar, 1979; Hetherington et al., 1986; Stueber et al., 1987; Kloppmann et al., 2001; Worden et al., 1999; Grobe and Machel, 2002). The strontium isotopic values for Group 3 range between 0.70872 and 0.71629 (Table 2). The strontium isotopic composition of Endmember 3 is 0.70911, which is comparable to the strontium signature of Paleozoic seawater. Paleozoic seawater has a strontium isotopic composition between 0.7070 to 0.7091 (Burke et al., 1982). The concentration of strontium for Group 3 ranges widely from 310 mg/l to 1700 mg/l.

Discussion

The systematic variations in the oxygen and hydrogen isotopic composition and salinity indicate distinct origins for Endmembers 1, 2 and 3. In Chapter 2 it was established that the observed close correspondence of

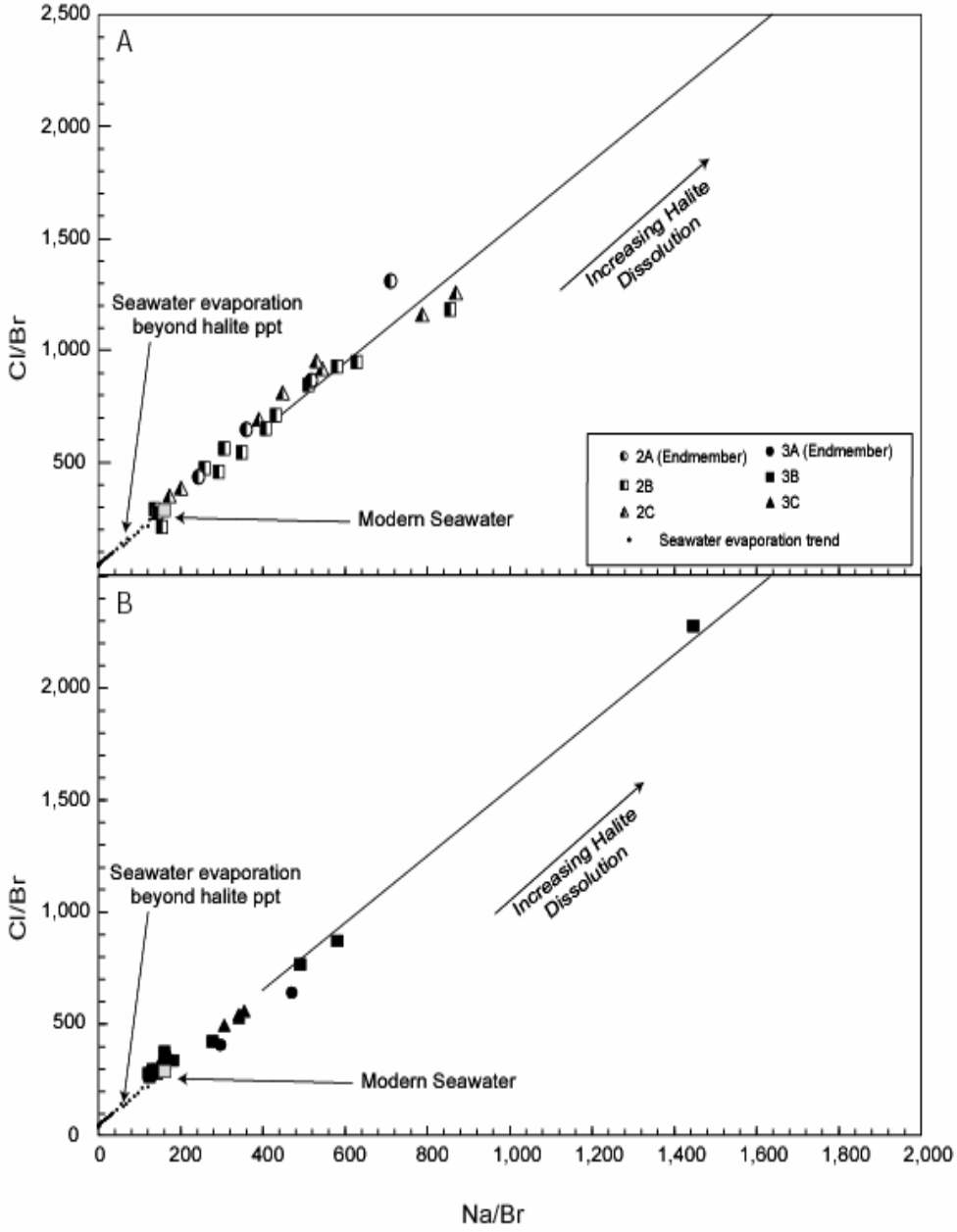


Fig. 3.5. Na/Br -Cl/Br relationship for groundwaters in the mid-continent. Groundwaters for Chaudhuri (1987, 1992) and Nicastro (1983) were not plotted due to lack of Br data. Small black circles denote seawater evaporation path from Gogel (1981). Cl/Br and Na/Br are expressed in weight ratios. (A) Group 2 groundwaters fall along the increasing dissolution trend. (B) Group 3 groundwaters plot along the seawater evaporation line and increasing halite dissolution. The scatter in the groups could be due to mixing of Groups 2 and 3. Group two has a higher Na/Br ratio than Group 3. Seawater is identified by the gray square. The use of these relationships was first presented by Walter et al. (1990)

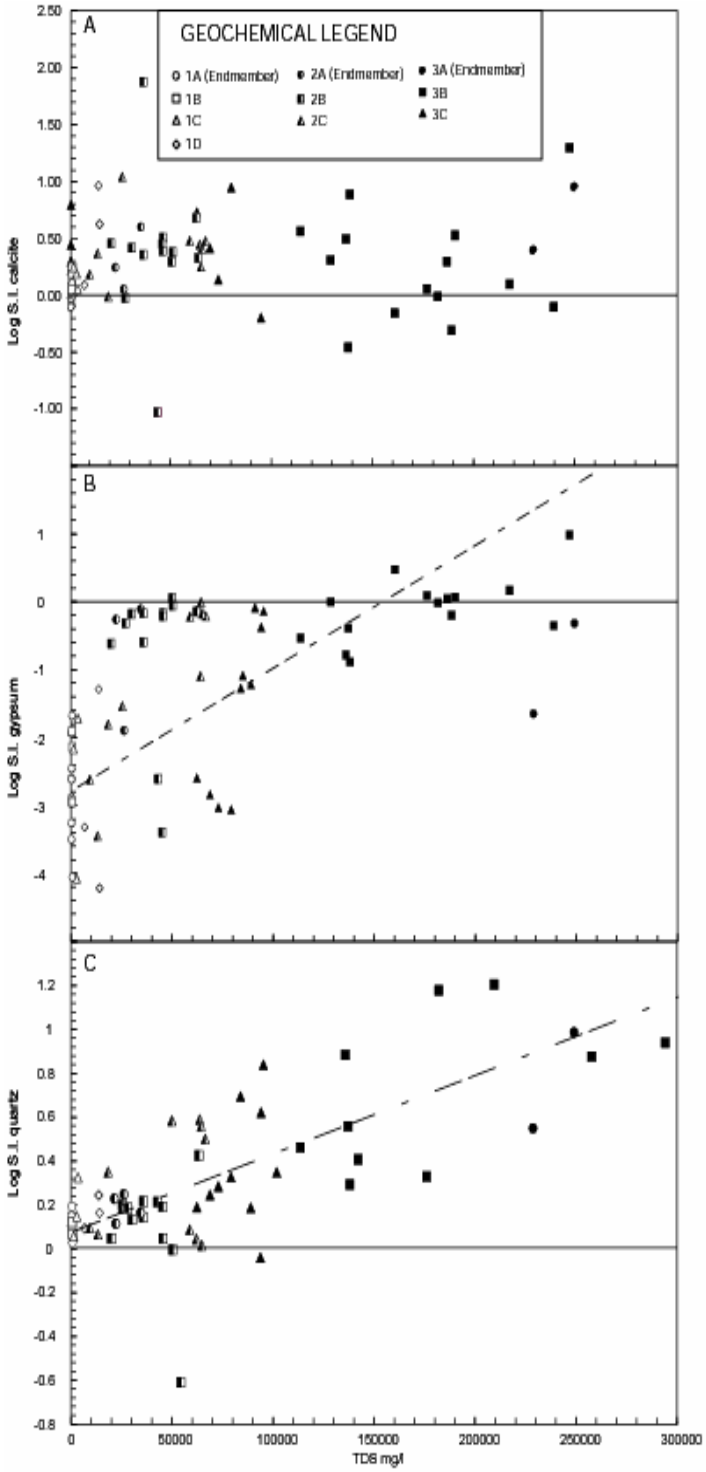


Fig. 3.6. Logarithm of saturation indexes of calcite, gypsum, and quartz versus total dissolved solids for WIP groundwaters. Indices calculated with NETPATH (Plummer et al., 1991). Most samples samples are oversaturated with respect to calcite and quartz and undersaturated with respect to gypsum. Saturation indices for groundwater samples from Chaudhuri (1987, 1992) and Nicastro (1983) were not calcuated due to lack of data. It can be observed in figures B and C a correlation, depicted by the dashed lines, between increasing TDS with increasing SI from Endmber 1A to Endmember 2A to endmember 3A, suggesting mixing and or water:rock interaction is affecting the geochemical character of the different groups.

geochemical variations, flow patterns and sample localities demonstrate that fluid mixing involving the endmember waters are controlling the composition of groundwater in the WIP.

Chloride and δD data for this area indicate that mixing involves all three groups (Figs. 2.3, Chapter 2). Chloride and δD data for south-central Kansas, southwest Kansas, eastern Colorado, and the Oklahoma panhandle indicate that these waters are chemically and isotopically similar to the groundwaters in southeastern Kansas, southwestern Missouri, and northeastern Oklahoma (Fig. 2.3B, Chapter2). Fluid mixing modeling for south central Kansas, southwestern Kansas, eastern Colorado, and the Oklahoma panhandle suggests that these groundwaters are the result of mixing between endmember 2A and 3A and a fresh water endmember (Fig. 2.3C, Chapter 2). The potentiometric surface map shows that Endmember 1A cannot be the fresh water component since it does not flow further than southeast Kansas (Fig. 3.7A). The westernmost boundary of the Ozark Plateaus aquifer system is defined by the geochemical transitional zone where Group 1 meets Group 2 (Musgrove, 1992). An alternate fresh water endmember could be groundwater from the GP (Fig. 2.3C, Chapter 2). This groundwater could infiltrate to the WIP via cross formational flow across the Pennsylvanian shales.

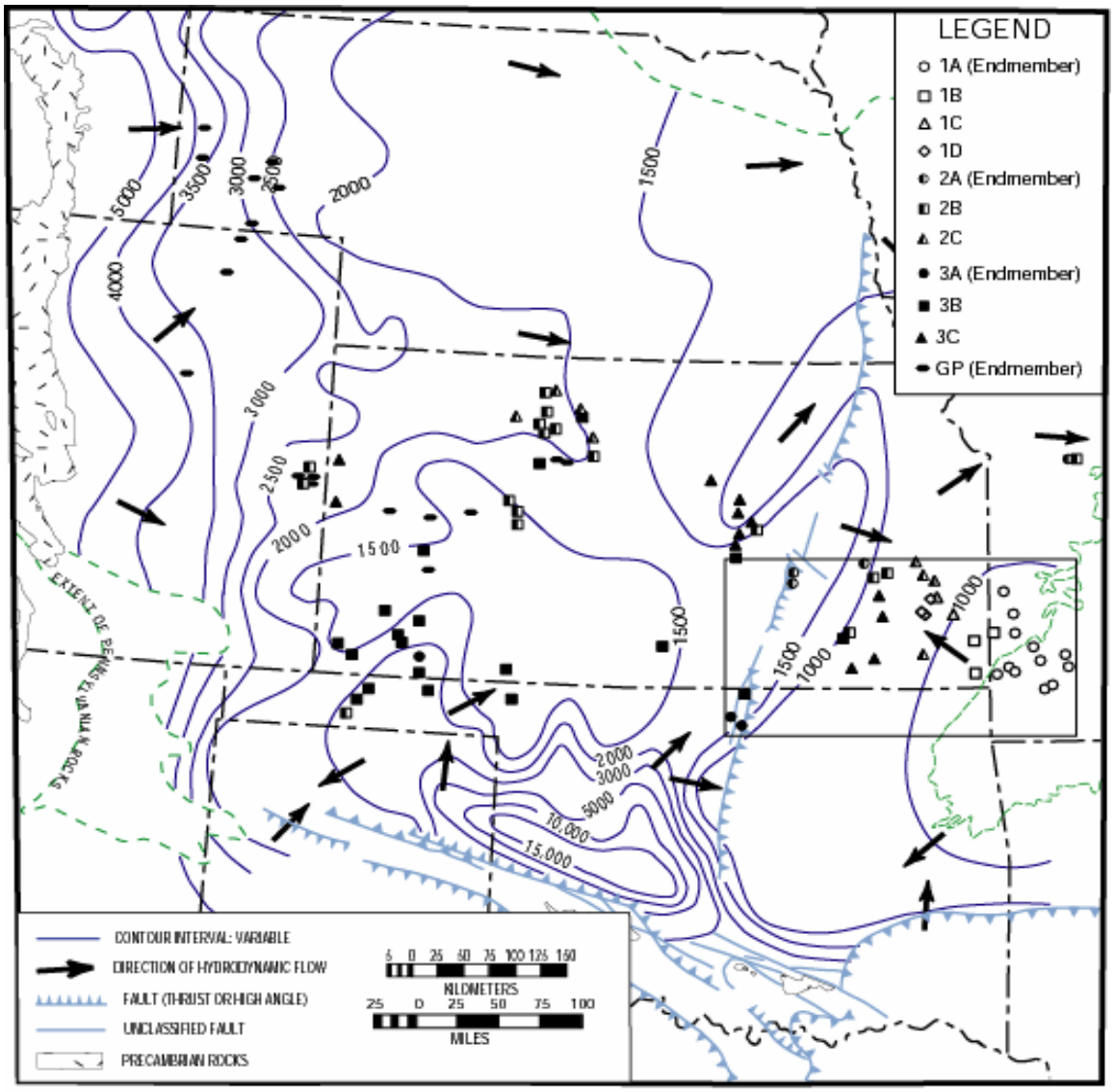
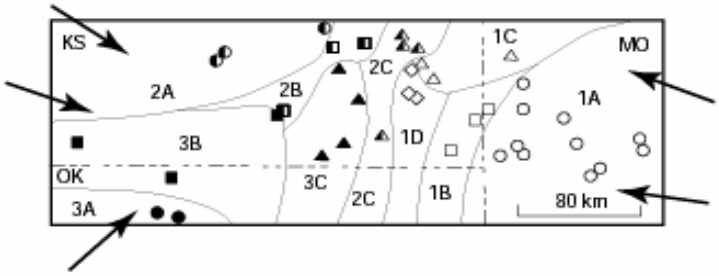


Fig. 3.7A Head difference map with group location. Box around samples from Musgrove and Banner (1993) in southwestern Missouri, southeastern Kansas, and northeastern Oklahoma is enlarged in figure 6B. Flow directions are based on head difference countour lines modified from T. G. Larson, 1971

Fig. 3.7B Close up of study area from Musgrove and Banner (1993). In this area there is a close correspondence between flow direction, geographic position, and water chemical and isotopic composition. Positions of boundary lines are based on sample localities and geochemical characteristics. Arrows represent regional flow diretion.



High-calcium groundwater

Groups 2 and 3 waters are Na-Ca-Cl. According to Carpenter (1978) high calcium content in the groundwater could be due to dolomitization through the following equation:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \quad (1)$$

An alternate source of high calcium concentrations could result from the albitization of feldspars at the expense of sodium through the following reaction:

$$CaAl_2Si_2O_8 + 4H_4SiO_4 + 2Na^{+} = 2NaAlSi_3O_8 + Ca^{2+} + 8H_2O \quad (2)$$

Calcium concentrations resulting from this process are limited by laumonite saturation (Land, 1987). In equation 2, two sodium ions are consumed for every calcium ion released, while conserving the amount of aluminum in solution. The availability of additional calcium in solution may result in precipitation of calcite cement, gypsum or anhydrite. The sulfate content in Group 3 groundwaters ranges between 2.6 to 2,600 mg/l. The equivalent evaporated seawater has a sulfate concentration of 17,600 mg/l; therefore suggesting that sulfate is being removed from solution. According to Orr (1974) sulfate may also be lost from Group 3 groundwaters through sulfate reduction via:

$$SO_4^{2-} + CH_4 = H_2S + CO_2 + 2OH^- \quad (3)$$

The low Eh values measured in Group 3 groundwaters in northeastern Oklahoma and southeastern Kansas suggest reducing conditions, which would be consistent with sulfate being reduced to H_2S (Appendix B). Eh values are particularly hard to obtain, however these can still be used in a qualitative mode to provide some general idea of reducing vs. oxidizing conditions. The loss of H_2S from the groundwaters may occur via the precipitation of pyrite (Carpenter, 1978). Finally, the loss of sulfate must be accompanied by the loss of cations to maintain electrical neutrality.

Davisson and Criss (1996) introduced a mathematical transformation of Na, Ca, and Cl concentrations that results in a unit slope between milliequivalents of Na and Ca. This transformation compares the excess calcium and the Na deficit relative to seawater. The excess Ca and the Na deficit are defined by Davisson and Criss (1996) as:

$$Ca_{excess} = \left[Ca_{meas} - \left(\frac{Ca}{Cl} \right)_{sw} * Cl_{meas} \right] * \frac{2}{40.08} \quad (4)$$

$$Na_{deficit} = \left[\left(\frac{Na}{Cl} \right)_{sw} * Cl_{meas} - Na_{meas} \right] * \frac{1}{22.99} \quad (5)$$

where the concentrations are in mg/l of ions measured (meas) are compared to those ions in seawater (sw) and these numerical constants are then converted into meq/l. These authors plotted Ca_{excess} vs $Na_{deficit}$ values for more than 800 basinal fluids in different aquifers and aquifer lithologies and derived a highly correlated regression line, called the basinal fluid line (BFL):

$$Ca_{excess}=0.967*(Na_{deficit})+140.3 \quad (6)$$

where the unit slope is suggested to indicate the albitization of plagioclase, which has a two Na for one Ca exchange ratio, is thought to be the main reaction controlling the chemistry of deep basinal fluids.

In a plot of Ca_{excess} vs $Na_{deficit}$ distinct trends for the different processes that affect saline groundwaters can be observed (Davisson and Criss, 1996). For the WIP samples it can be observed that Group 3 groundwaters plot along the BFL trajectory suggesting that those water are affected by the albitization of plagioclase, which would require a 2:1 exchange of Na for Ca (Fig. 3.8). An example of this reaction is presented in equation 2. It can also be observed in this plot that some of the Group 2 samples fall along the halite dissolution trend. It can also be observed for this group that there is an increase in the Ca_{excess} without or very little change in the $Na_{deficit.}$, suggesting the dissolution of $CaCO_3$ and $CaSO_4$ and dolomitization of calcite.

Evidence for water-rock interaction

Fluid mixing can closely account for most of the variability among conservative geochemical tracers such as H and O isotopes and Cl concentrations of the groundwater in the WIP (Chapter 2), however it can not account for the strontium isotope variations seen in the intermediate (i.e. non-

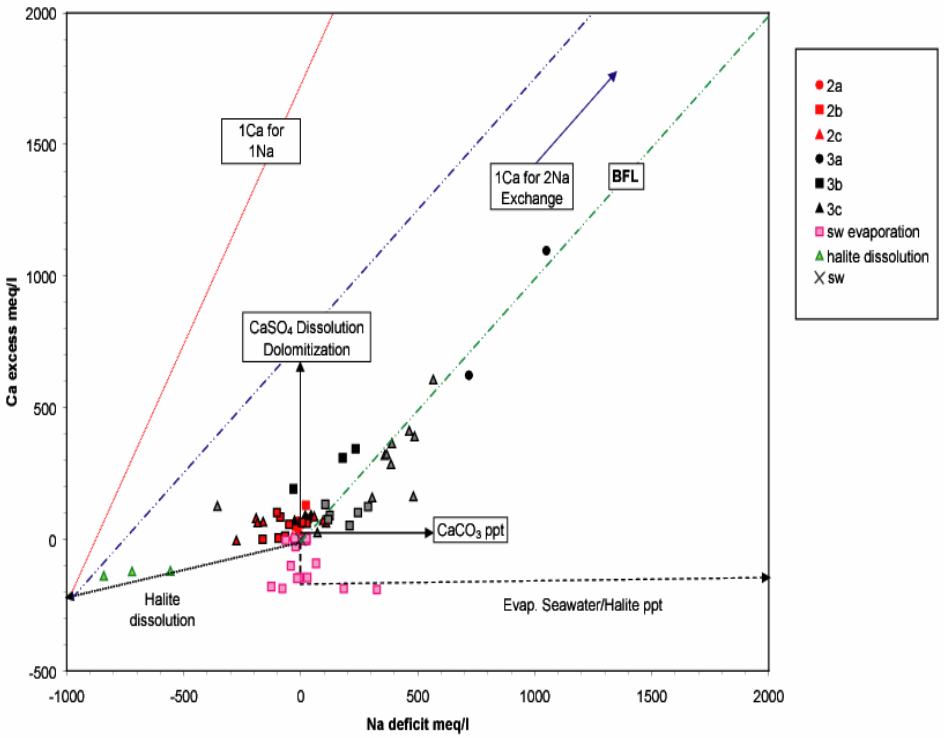


Fig 3.8. Processes affecting the Group 2 and Group 3 groundwaters in the WIP can be explained by the relationship between Ca excess and Na deficit. Ca excess and Na deficit are a mathematical transformation that allows the comparision between the excess in Ca and the deficit in Na with respect to seawater. BFL, stands for Basinal fluid line, and it is a linear regression with a slope of one on the excess deficit plot. Davisson and Criss (1992) after plotting more than 800 samples that most basinal fluids conform to this one-to-one slope. Ca excess and Na deficit relationship was described by Davisson and Criss (1992).

values together with very high strontium concentrations suggest extensive water-rock interaction with a relatively non-radiogenic source of strontium. A likely source is Mississippian carbonates from Kansas, Iowa, Illinois, and Missouri,

which exhibit $^{87}Sr/^{86}Sr$ values ranging from 0.7078 to 0.7122 (Chaudhuri et al, 1987; Banner et al., 1988) (Fig. 3.9). The model simulations based on H and O isotope and Cl concentration variations in WIP groundwater cannot account for a significant amount of the Sr isotope variability, especially for Group 2 groundwater (Fig. 3.10). It can be observed that both endmembers 1A and 3A are still the geochemical endmembers for those groups; however, Endmember 2A is no longer an endmember. This could mean that Endmember 2 has been significantly affected by water:rock interaction or that it is not an endmember, but an intermediate member. If the latter is correct, that would mean that the Endmember for Group 2 is yet to be found. Most notably, the results of fluid-mixing modeling, using the three WIP endmembers, of the δD -strontium variability in the WIP yield model Sr isotope values for Group 2 waters (e.g., "Mix 2-3" curve in Fig. 3.11) that are significantly lower than the measured values in these waters. The results of fluid mixing modeling using hydrogen and strontium isotopes indicate that the composition of Group 2 groundwater is not just the result of mixing but that also involves other processes such as water:rock interaction (Fig. 3.11). This modeling uses the same endmembers from the δD-Cl modeling presented in Chapter 2.

The strontium isotopic ratios for Group 2 range from 0.70898 to 0.72372. These values are higher than the strontium isotopic signature for Paleozoic seawater, which ranges from 0.7070 to 0.7091 (Burke et al, 1982). Chaudhuri et al. (1987) measured the strontium isotopic ratio of Pennsylvanian clays and

leachates from the clays. Potassium: rubidium ratios can provide clues as to the degree of water: rock interaction. Formation waters are usually depleted in

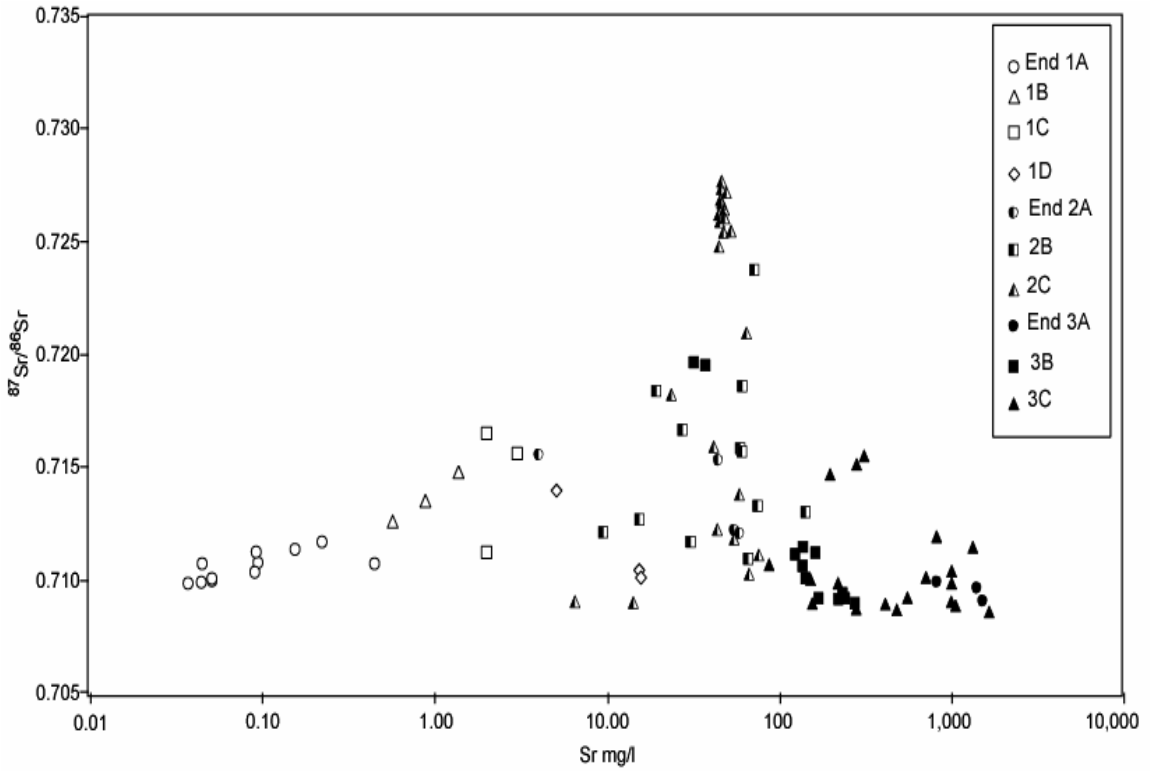


Fig. 3.9 Plot of strontium concentration vs strontium isotopic composition. It can be observed that while Endmembers 1 and 3 are still the pristine groundwaters for their respective groups, Endmember 2 is no longer a true endmember. This suggests that the geochemical composition of Endmember 2 and Group 2 is not only the result of mixing but is also affected by water:rock interaction.

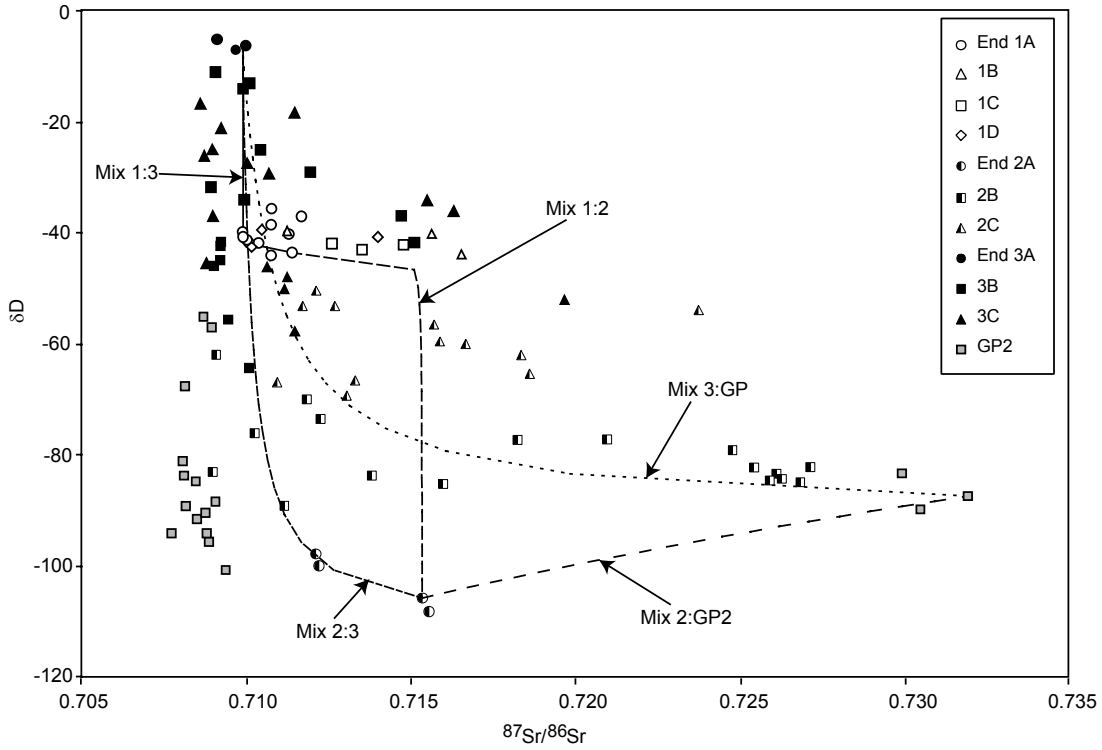


Fig. 3.10 Model results of mixing between the three WiP endmembers and the GP2 endmember. This model used the same endmembers used to modelCl vs dD. The mixing curves in this plot do not account for all the data, suggesting that mixing is not the only process altering the chemistry of these groundwaters, water:rock interaction seems to have a signifcant role in the final chemistry of these groundwaters.

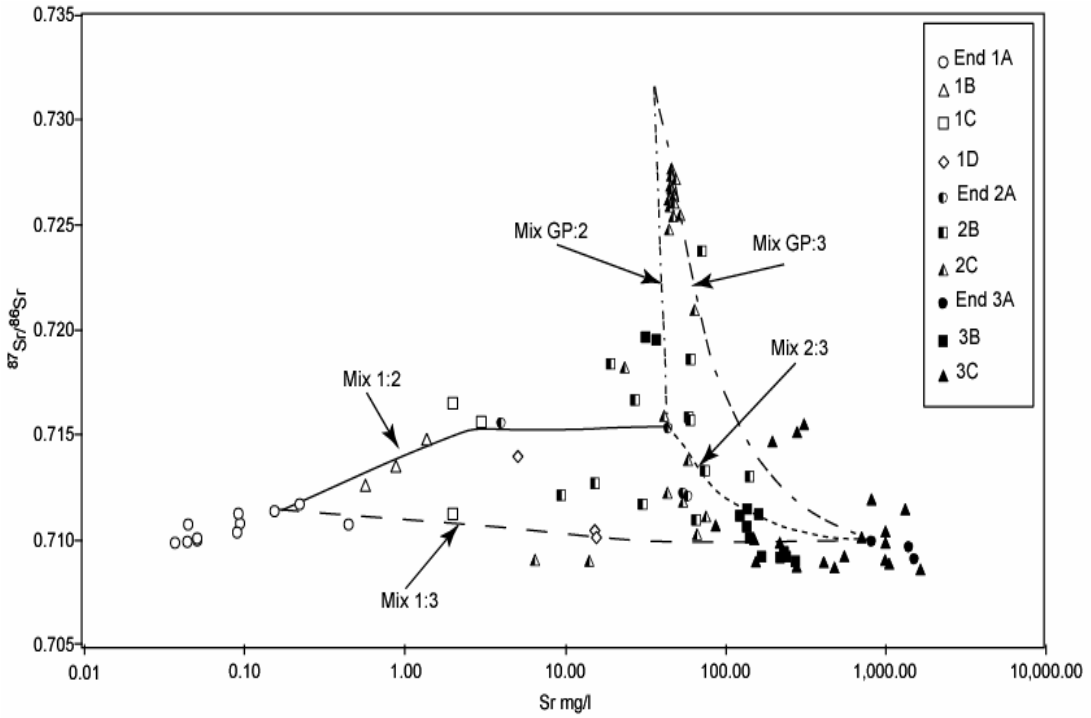


Fig. 3.11. Modeling mixing results for the WIP groundwaters. This model uses the same endmembers from δD-Cl modeling. This was done to closely account for the variability of the data. It can be observed that simple mixing between the 3 endmembers does not account for all the data. If groundwater from the Great Plains is used as an endmember then most of the data can be accounted for.

K but enriched in Rb relative to evaporated seawater (Chaudhuri and Clauer, 1993). Typically the K/Rb ratio for formation water in sedimentary basins range from 200 to 2000. Groups 2 and 3 have K/Rb ratios ranging from 355 to 1216 (Chaudhuri and Clauer, 1993; Fig. 3.12; Table 3.2). The WIP groundwater samples with the lowest K/Rb ratios are the samples with the highest strontium isotopic signature (Fig. 3.13). This suggests that those samples have undergone the highest degree of water:rock interaction. K/Rb ratios of most sedimentary basin waters range between 200 and 2,000 mg/l, which is different from the K/Rb ratios of seawater, river water, K-feldspar, plagioclase, halite and sylvite (Fig. 3.12; Chaudhuri and Clauer, 1993). This ratio can be affected by the albitization of plagioclase or K-feldspar. Additionally, the transformation of smectite to illite during deep burial can affect the budget of K and Rb (Chaudhuri and Clauer, 1993).

Water-rock interaction modeling

Water:rock modeling was undertaken in order to ascertain if the isotopic signature of the radiogenic groundwaters within Group 2 is the result of interaction with clays in the overlying strata or interaction with the granitic basement, and to help determine the source of the salinity for Group 2 (Table 3.3). Using methods outlined in Banner and Hanson (1990), an iterative calculation is used to simulate isotopic and elemental exchange during dissolution-recrystallization of a carbonate aquifer by a groundwater. Four different scenarios were modeled, 1) granite interacted with a groundwater with

high strontium isotope composition, 2) granite interacted with a groundwater with low strontium isotope composition, 3) Pennsylvanian clay interacted with a groundwater with high strontium isotope composition, and 4) Pennsylvanian clay interacted with a groundwater with low strontium isotope composition (Table 3.4) All the models above were run with calcite and for 100,000 iterations. Iteration is a computational procedure, in which a cycle of operations is repeated,
The strontium isotopic composition of the groundwater achieves isotopic equilibrium at a high water: rock ratios in all four scenarios (Fig. 3.14). Groundwater equilibrates with the rock quickly because the strontium concentration of the rock is higher than the strontium concentration and the strontium isotopic composition of the rock is much higher than that of the fluids (Table 3.3).

More than one process could be working in the mid-continent; for example, interaction with the granitic basement, close to the Nemaha Uplift or the Central Kansas Uplift would result in a high Sr isotopic signature in groundwater. In areas of the mid-continent between structural highs or faulting, the high Sr isotopic signature could be the result of groundwater interaction with shales or groundwater from the GP that is now mixing with the WIP. Groundwater from the

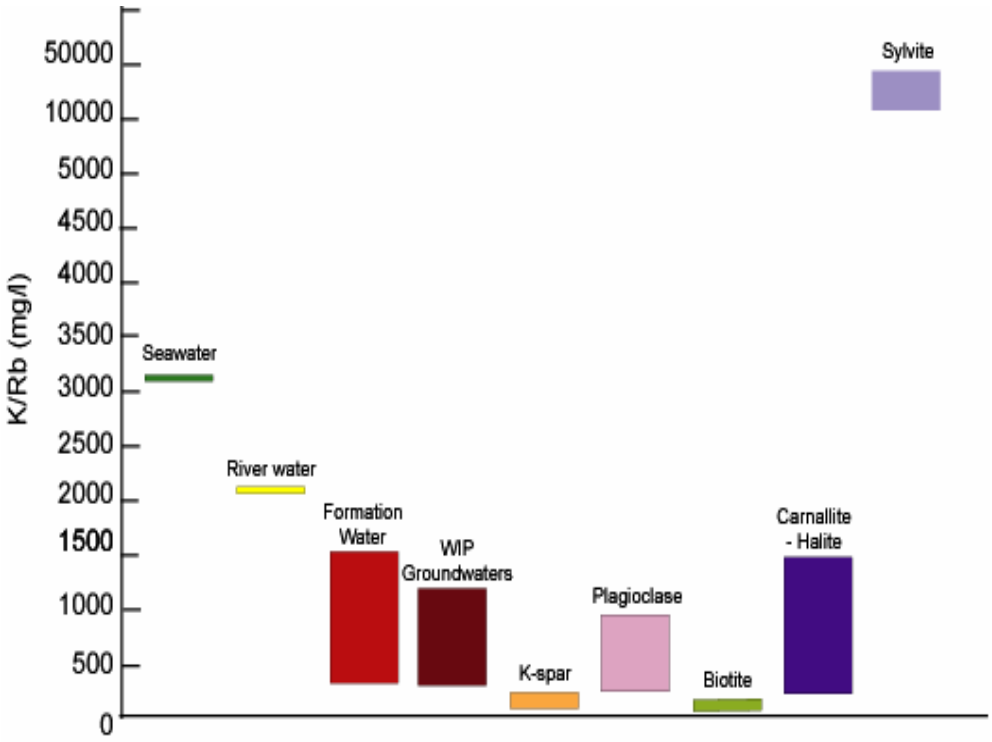


Fig. 3.12 K/Rb ratios of formation waters, surface waters, evaporites and some common K-bearing silicate minerals. Figure was modified from Chadhuri and Clauer, (1993)

GP would be infiltrating through the Pennsylvanian shales and acquiring a high signature from the shales. A radiogenic strontium signature within the fluid can be achieved by interacting with argillaceous components within the rock. The origin of the high strontium isotopic signature could be due to the dissolution and replacement of detrital alkali feldspar and micas and the illitization

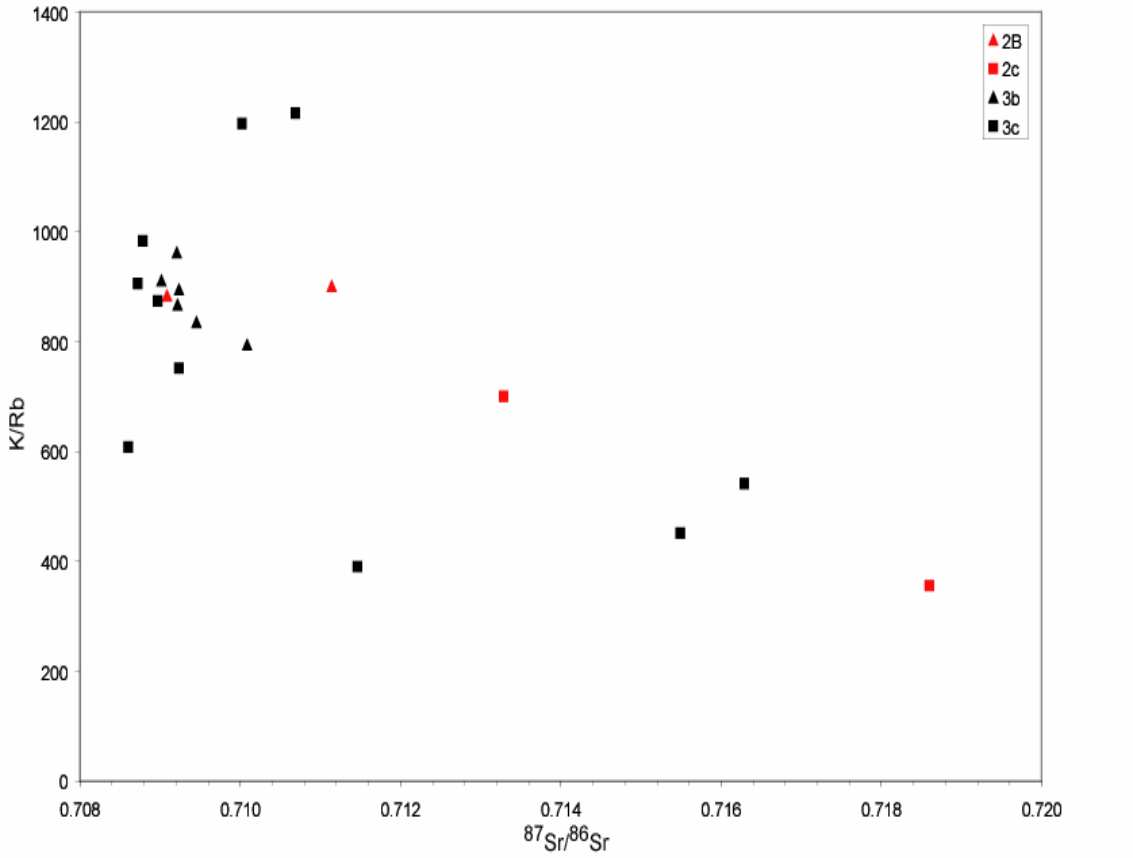


Fig. 3.13. K/Rb and Sr isotope variations in WIP groundwaters. Note inverse correlation between these parameters. Rb data was not available in Musgrove (1993), Chadhuri (1987, 1992), and Nicastro (1983).

Table 3.4 – Rock and water samples used to model rock-water interaction

	Sr mg/l	Ca mg/l	$^{87}Sr/^{86}Sr$	$\delta^{18}O$ SMOW	T °C
Granite	14	NA	0.8793	22	
Pennsylvanian Clay	14	NA	0.79508	22	
Paleozoic carbonate	80	NA	0.707	27	
Warren #1	71	2366	0.72372	-4	35
Regier #1	1700	9900	0.7086	1.4	25

Four scenarios were modeled. Warren #1 was reacted with whole clay, and with Paleozoic carbonate. Regier #1 was reacted with Pennsylvanian clay. $K_D^{Sr\text{-}Ca}$ for calcite was 0.05. The granite, Pennsylvanian clay and Paleozoic data are from Giletti and Casserly (1994), Chaudhuri and Clauer (1993), and Musgrove (1993).

of smectites (Chaudhuri and Clauer, 1993). Albitization of plagioclase could be one of the main processes by which groundwaters acquire a high strontium isotopic signature (Chaudhuri and Clauer, 1993). This process involves either the direct replacement of K-feldspar or the replacement of K-feldspar by some other mineral, such as calcite or anhydrite, which in turn are replaced by albite (Chaudhuri and Clauer, 1993).

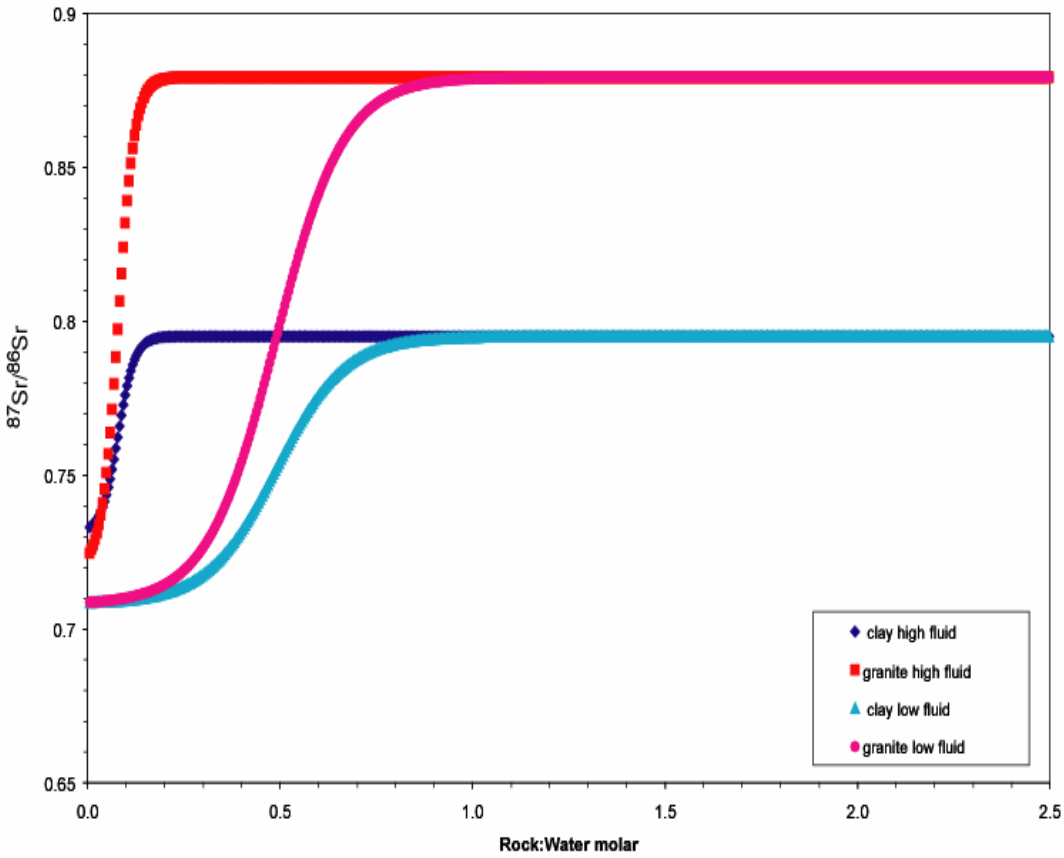


Fig. 3.14. Results of rock-water interaction modeling between clay and groundwater and granite and groundwater. These simulations were done twice, first with a radiogenic groundwater as an endmember and second with a non-radiogenic groundwater. The fluids with low strontium isotopic values also had low strotnium concentrations. It can be observed that the groundwater equilibrates with either clay or granite after a low extent of rock:water interaction, this is controlled by the strontium concentration of the groundwater sample and by the high strontium isotopic composition of granite and the clays. The endmembers, i.e. low fluid vs high fluid, are groundwaters from the WIP with the highest or lowest strontium isotopic signatures.

Spatial distribution of groundwater types

It can be observed that groundwater in the WIP has a distinct regional geographic extent (Fig. 3.15A). Group 1 groundwaters are primarily found in southwestern Missouri and southeastern Kansas (Fig. 3.15A). Group 2 groundwaters are found in northern Kansas and western-central Missouri (Fig. 3.15A). Group 3 groundwaters are present in south central Kansas, southwest Kansas, and the Oklahoma panhandle (Fig. 3.15A). In central-west Kansas there is a significant degree of chemical and isotopic heterogeneity in a small area, in which groundwater types 2B, 2C, and 3C have been found (Fig. 3.1). This heterogeneity in such a small area suggests that several processes are affecting the chemical character of the groundwaters. All of these wells are located close to the central Kansas uplift and from the potentiometric surface map we can see that the majority of these wells are within an area of no flow or very sluggish flow (Fig. 3.7A).

The Paleozoic formations on the Central Kansas uplift onlap over Precambrian granite rock due to the structural development of the Central Kansas Uplift (Chaudhuri et al, 1987). This onlap would increase the intensity of water:rock interaction of the waters flowing from the uplift since the groundwaters would be in direct contact with the Precambrian granite. The water:rock interaction would be evidenced in the chemical composition of the groundwaters.

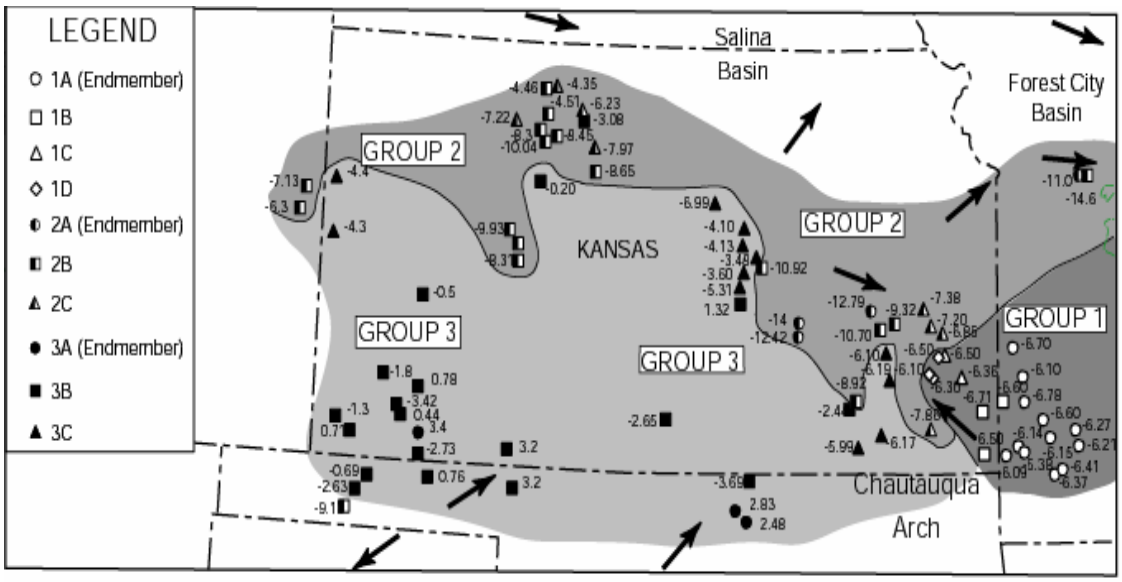


Fig. 3.15A Close up of the study area showing group location and regional extent of groups and oxygen delta values. The regional extent of the groups is based on sample localities and geochemical characteritics. Boundary lines are only places where there is data control. Both figures 3.15A and 3.15B have the same scale. Arrows depict direction of flow.

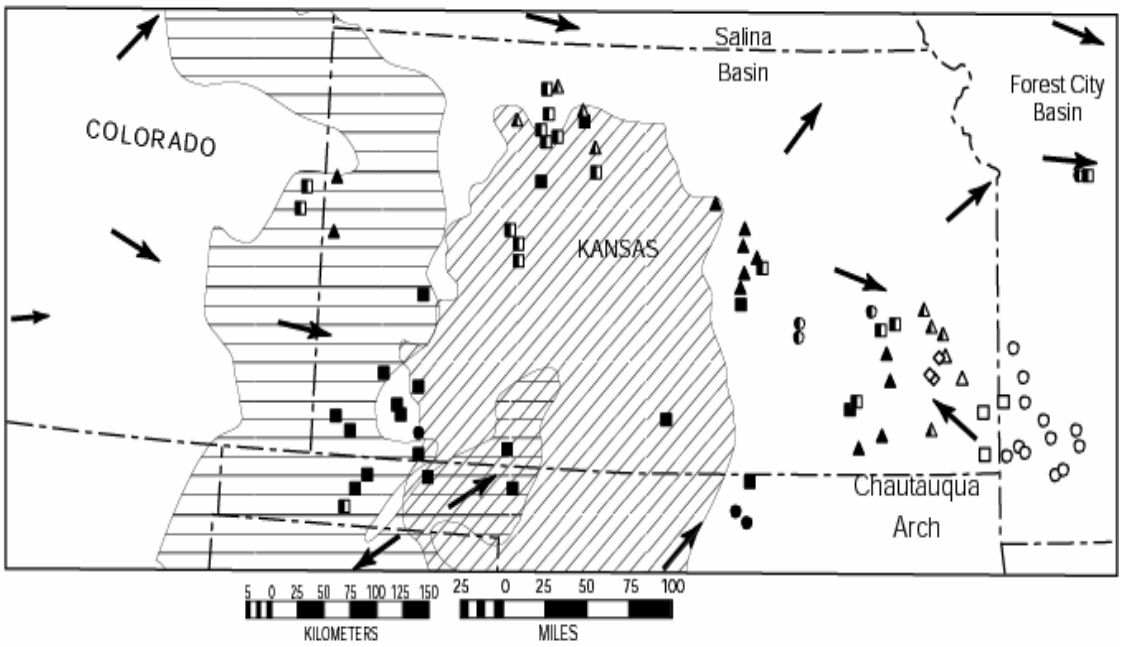


Fig. 3.15B Extent of the Nipewalla formation (horizontal lines) and the Hutchison Salt Member of the Wellington Formation (diagonal lines). Both of these evaporite units are Permian in age. The Nipewalla Group consists of several units described in the text. Group 2 samples east of the Hutchison salt Member probably acquired their salinity from the evaporite units within the Nipewalla Group. The remainder of group 2 salinity is probably derived from both evaporite sequences. Groundwater group legend for this figure is given in Fig. 3.15A.

Origin of salinity in Groups 2 and 3 groundwater

Three processes can produce saline fluids in a sedimentary basin, 1) shale membrane filtration, 2) subaereal evaporation of seawater, and 3) subsurface dissolution of evaporites (Hanor, 1987). Land (1995) stated that shale membrane filtration fails to explain many geochemical observations, such as the fact that an increase in Ca concentration should be accompanied by an increased in other divalent ions such as Sr and Ba. Additionally, this process has yet to be proven to work on a large scale area, such as the Illinois basin (Hanor, 1987). Based on the shortcomings of the shale membrane filtration model, it will not be considered further as one of the processes that could generate the salinity in the WIP. A more detailed description on shale membrane filtration can be found in Chapter 2.

The Br-Cl trend for Group 2 groundwater lies below seawater and the seawater evaporation trajectory (Fig. 3.4). The low bromide and chloride concentrations of Group 2 compared to seawater suggest that the salinity could result from halite dissolution. Group 2 groundwaters are considerably more dilute than the brines resulting from the dissolution of Permian halite in central Kansas (Fig. 3.5A). Group 2 brines fall within the dilution of halite dissolution brines field, suggesting that these brines have been diluted through mixing with Group 1 as shown in Chapter 2. Additionally, the Na/Br-Cl/Br relationship indicates that the composition of Group 2 samples resulted from halite dissolution (Fig. 3.5A).

There are two main evaporite-bearing units in the in the study area, the Hutchison Salt Member of the Wellington Formation, and the Nipewalla Group (Fig. 3.15B). Both evaporite deposits are Permian in age. The Nipewalla Group consists of red bed-evaporite sequences (Holdoway, 1978). In ascending stratigraphic order the group consists of the Harper and Salt Plain formations, Cedar Hill sandstone, Flower-pot shale, and Blaine Formation. The main sediments in the group are red clay, silt and sand, varying amounts of halite and anhydrite, and minor amounts of dolomite, magnesite, and quartz (Holdoway, 1978). Halite is the most abundant evaporite in the Nipewalla Group, particularly in the Flower-pot shale and Blaine Formation. In the Flower-pot, halite makes up 80% of the sediments with red silty mudstone making up the reminder of the section. The Blaine Formation is the only unit that has relatively pure halite free of mudstones and siltstones. The halite in the Blaine Formation is interbedded with anhydrite.

The salinity of Group 2 groundwaters in eastern Colorado probably results from the dissolution of evaporites within the Nipewalla Group (Fig. 3.15B). For the remainder of the group located to the east, the salinity probably originates from the dissolution of the Hutchison Salt Member and/or Nipewalla Group evaporites.

While both Groups 2 and 3 are Na-Ca-Cl waters, Group 3 has higher Ca concentrations and salinities (Fig. 3.3). Groundwaters form Group 3 also have very little SO_4 compared to Group 2 (Fig. 3.3). $\delta^{18}O$ isotope values for Group 3 are several per mil enriched with respect to seawater while δD are similar to

those from seawater (Fig. 2.4, Chapter 2). Group 3 chemical and isotopic variations are very similar to fluid inclusion brines in Permian salt in Central Kansas. This is consistent with Group 3 compositions resulting from the evaporation seawater. The relatively low strontium isotopic values for Group 3 could be explained by water:rock interaction with host carbonate aquifer rocks and limited mixing with fluids from the Pennsylvanian shales.

The degree of evaporation of a brine is expressed as the ratio of the weight of the water in the original seawater to the weight of the water in the residual evaporated brine (Knauth and Beeunas, 1986). Br and Cl concentrations of Endmember 3 correspond to a degree of evaporation between 9 and 10.5 (McCaffrey et al., 1987). Group 3B corresponds to a degree of evaporation between 3 and 8.5 while Group 3C corresponds to a degree of evaporation ranging between 2.6 and 3.5 (McCaffrey et al., 1987). The lesser degree of evaporation observed in Groups 3B and 3C is more likely due to mixing with Groups 1 and 2, rather than to differing extents of evaporation. Calcium carbonate begins to precipitate at a degree of seawater evaporation of 1.8, the onset of gypsum precipitation is at a degree of evaporation of 3.8, and halite begins to precipitate at a degree of evaporation of 10.6 (McCaffrey et al., 1987). This degree of evaporation suggests that Group 3 could be precipitating $CaCO_3$ as calcium carbonate cement. Only Groups 3B and 3A could precipitate gypsum. This is consistent with the relatively low sulfate content in Groups 3B and 3A compared to equivalent evaporated seawater.

Additionally, Br-Cl systematics for Group 3 are consistent with a marine origin (Figs. 3.5A, 3.5B). Na/Br-Cl/Br relationships for Group 3 are consistent with a seawater origin, while the Br-Cl relationship for this group falls within the evaporated seawater trend, supporting the evaporated seawater origin. The scatter of the data within Group 3 is likely the result of mixing with Group 1 and Group 2 groundwater. A summary of the geochemical and isotopic characteristics of Groups 2 and 3 that were used to evaluate the origin of the salinity, sources of recharge, water:rock interaction can be found in Table 3.5.

Table 3.5 Summary of major characteristics for Groups 2 and 3 used to determine the origin of the salinity, water type, and water:rock interaction

Group	**Group 2**	**Group 3**
Water type	Na-Ca-Cl	Na-Ca-Cl
Salinity	Intermediate	High
Br/Cl	Low	High
SO_4	High	Low
Ca	Low to intermediate	High
Strontium isotopic composition	Radiogenic, indicative of interaction with silicates	Non-radiogenic, similar to Paleozoic seawater values and values indicative of interaction with marine carbonates
Oxygen and hydrogen isotopic composition	Low Along the MWL	High Off the MWL
Origin of salinity	Dissolution of Permian evaporites and subsequently modified by water:rock interaction	Evaporation of seawater and subsequently modified by water:rock interaction

Conclusions

Br-Cl-Na-Ca systematics, together with stable isotopes of H and O and strontium isotopes, are used to investigate the origin of saline fluids in the WIP. The groundwaters from the Western Interior Plains aquifer system in the mid-continent exhibit a wide range of chemical and isotopic variability that reflect large scale fluid mixing. Three main water types found in the mid-continent are Groups 1, 2, and 3. Group 2, in northern Kansas, eastern Colorado, and central-western Missouri is characterized as a Na-Ca-Cl saline brine. The salinity of Group 2 could be due to the dissolution of the Hutchison Salt Member and the evaporites in the Nipewalla Group. The high strontium isotopic composition of this group can be due to interaction with the Precambrian basement at structural highs or faults or mixing with fluids that have been in contact with shales, possibly the Pennsylvanian shales. Group 3 is also a Na-Ca-Cl brine originating in the Anadarko Basin. The salinity of this group could be due to the evaporation of seawater. The geochemical character of this groundwater also could have been modified by albitization of plagioclase or K-feldspar.

References

Banner, J. L., Wasserburg, G. J., Dobson, P. F., Carpenter, A. B., and Moore, C. H., 1989, Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri, Geochimica and Cosmochimica Acta, Vol. 53, pp. 383-398.

Banner, J. L. Hanson, G. N., and Meyers, W. J., 1988, Determination of initial Sr isotopic compositions of dolostones from the Burlington-Keokuk Formation (Mississippian): Constraints from cathodoluminescence, glauconite paragenesis and analytical methods, J. Sediment. Petrol, Vol, 58, pp. 673-687.

Banner, J. L. and Hanson, G N., 1990, Calculations of simultaneous isotopic and trace element variations during water:rock interaction with applications to carbonate diagenesis, Geochimica et Cosmochimica Acta, Vol. 54, pp. 3123-3137.

Bethke, C. M., 1994, The Geochemist's Workbench, version 2.0, A users guide to Rxn, Act2, Tact, React, and Gtplot, Hydrogeology Program, University of Illinois.

Bethke, C. M., and Marshak, S., 1990, Brine migration across North America – The plate tectonics of groundwaters, Annu. Rev. Earth Planet. Sci., Vol. 19, pp. 287-315.

Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982, Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time, Geology Boulder, Vol. 10, Issue 10, pp. 516-519.

Carpenter, A. B., 1978, Origin and chemical evolution of brines in sedimentary basins, Oklahoma Geological Survey Circular 79, pp. 60-70.

Chaudhuri, S., Broedel, V., and Clauer, N., 1987, Strontium isotopic composition of oil-field waters from carbonate reservoir rocks in Bindley field, central Kansas, U.S.A., Geochimica et Cosmochimica Acta, Vol. 51, pp. 45-53.

Chaudhuri, S., and Clauer, N., 1993, Strontium isotopic compositions and potassium and rubidium contents of formation waters in sedimentary basins:

Clues to the origin of the solutes, Geochimica et Cosmochimica Acta, Vol. 57, pp. 429-437.

Chaudhuri, S., Robinson, R., Clauer, N., and Jones, L. M., 1992, Evolution of formation waters in Early Pennsylvanian Morrowan sandstones in the Hugoton Embayment of the Anadarko Basin, southern Midcontinent, U.S.A., Oklahoma Geological Survey Circular 93, pp. 160-174.

Davisson, M. L. and Criss, R E., 1996, Na-Ca-Cl relations in basinal fluids, Geochimica et Cosmochimica Acta, Vol. 60, No. 15, pp. 2743-2752.

Dutton, A. R., 1994, Sources and ages of ground water in unconfined and confined aquifers beneath the U.S. high plains, Final technical report, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas.

Dutton, A. R. and Bein, A, 1993, Origin, distribution, and movement of brine in the Permian Basin (U.S.A.): A model for displacement of connate brine, GSA Bulletin, Vol. 105, pp. 695-707.

Epstein, S., and Mayeda, T.K., 1953, Variations of O^{18} contents of waters from natural sources, Geochimica and Cosmochimica Acta, Vol. 4, pp. 213-224.

Faure, G., 1986, Principles of isotope geology, 2nd Edition, 589 p. John Wiley & Sons publishers

Franz, R. H., 1985, Distribution of petrophysical properties in the lower Morrow sandstone (Keyes), southwest Kansas *in:* Watney, W. L., and Doveton, J. H., Core studies in Kansas, Kansas Geol. Surv. Subsurface Geol. Series, No. 6 pp. 56-65.

Giletti, B. J. and Casserly, J. E. D., 1994, Strontium diffusion kinetics in plagioclase feldspars, Geochimica et Cosmochimica Acta, Vol. 58, No. 18, pp. 3785-3793.

Gogel, T., 1981, Discharge of saltwater from Permian rocks to major stream-aquifer systems in central Kansas, Kansas Geological Survey, Chemical Quality Series No. 9, 60 p.

Grobe, M., and Machel, H. G., 2002, Saline groundwater in the Münsterland Cretaceous Basin, Germany: Clues to its origin and evolution, Marine and Petroleum Geology, Vol., 19, pp. 307-322.

Hanor, J. S., 1987, Origin and migration of subsurface sedimentary brines, SEPM Short Course No. 21, 247 p.

Hanor, J. S., 1983, Fifty years of development of thought on the origin and evolution of subsurface sedimentary brines: *in* Boardman, S. J. (ed.), Revolution in the Earth Sciences, Kendal Hunt Publishing Co., pp. 99-111.

Helgesen, J. O., Leonard, R. B., and Wolf, R. U., 1993, Hydrology of the Great Plains Aquifer System in Nebraska, Colorado, Kansas, and adjacent areas, USGS Professional Paper, 1414-E.

Hetherington, E. A., Stueber, A. M., and Pushkar, P., 1986, Strontium isotopic study of subsurface brines from Illinois Basin (Abstr.), Amer. Assoc. Petrol. Geol. Bull. Vol. 70, p. 600.

Holdoway, K. A., 1978, Deposition of evaporites and red beds of the Nipewalla Group, Permian, western Kansas, Kansas Geol. Survey Bull., No. 215, 43p.

Jorgensen, D. G., Helgesen J. O., and Imes, J. L., 1993, Regional aquifers in Kansas, Nebraska, and parts of Arkansas, Colorado, Missouri, New Mexico, Oklahoma, south Dakota, Texas and Wyoming-geohydrologic framework, USGS Professional Paper 1414-B.

Kloppmann, W., Négrel Ph., Cassanova, J., Klinge, H., Schelkes, K., and Guerrot, C., 2001, Halite Dissolution derived brines in the vicinity of a Permian salt dome (N. Germany Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes, Geochimica et Cosmochimica Acta, Vol. 65, No. 22, pp. 4087-4101.

Knauth, L. P. and Beeunas, M. A., 1986, Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters, Geochimica et Cosmochimica Acta, Vol. 50, pp. 419-433.

Land, L. S., 1987, The major ion chemistry of saline brines in sedimentary basins *in:* Banavar, J. R., Koplik, J., and Winkler, K. W., eds., International Symposium on Physics and Chemistry of Porous Media, 2nd, Ridgefield, Connecticut, 1986, Proceedings, New York, American Institute of Physics, No. 154, pp. 160-179.

Land, L. S., 1995, Na-Ca-Cl Saline formation waters, Frio Formation (Oligocene), South Texas, USA: Products of diagenesis, Geochimica et Cosmochimica Acta, Vol 59, No. 11, pp. 2163-2174.

Land, L. S., and Macpherson, G. L., 1992, Origin of saline formation waters, Cenozoic section, Gulf of Mexico Sedimentary Basin, AAPG Bulletin, Vol. 76, No. 9, pp. 1344-1362.

Larson, T. G., 1971, Hydrodynamic Relationships in the Mid-Continent *in*: Cram, I. H. (ed) Future Petroleum Provinces of the Mid-Continent – Their Geology and Potential, AAPG Memoir 15, Vol. 2, pp. 1043-1046.

McCaffrey, M. A., Lazar, B., and Holland, H. D., 1987, The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite, Journal of Sedimentary Petrology, Vol. 57, No. 5, pp. 928-937.

Miller, A., and Appel, C. L., 1997, Ground water atlas of the United States, Kansas, Missouri, and Nebraska, USGS, HA 730-D.

Musgrove, M., 1993, Origin, evolution, and mixing of saline and dilute groundwaters in three regional flow systems, Midcontinent, U.S.A., unpub. M.S., The University of Texas at Austin, 225 p.

Musgrove, M., and Banner, J. L., 1993, Regional ground-water mixing and the origin of saline fluids: Midcontinent, United States, Science, Vol. 259, pp. 1877-1882.

Nicastro, L., 1983, Isotopic and chemical studies of oil-field waters associated with Upper Paleozoic rocks, Miner field, Ness County, Kansas, unpub. M.S., Kansas State University, 89 p.

Orr, W. L., 1974, Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-study of Big Horn basin Paleozoic oils, AAPG, Vol. 58, No. 11, pp. 2295-2318.

Pierre, C., Ortlieb, L., and Person, A., 1984, Supratidal evaporitic dolomite at Ojo de Liebre lagoon: mineralogical and isotopic arguments for primary recrystallization, Jour. of Sed. Petrol., Vol. 54, No. 4, pp. 1049-1061.

Plummer, L. N., Prestemon, E. C., and Parkhurst, D. L., 1991, An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, USGS Water Resources Investigation Report 91-4078, 227 p.

Robinson, T. J., Chaudhuri, S., and Jones, L. M., 1985, Diagenesis of Pennsylvanian Morrowan sandstones, Clark county, Kansas *in:* Watney, W. L., and Doveton, J. H., Core studies in Kansas, Kansas Geol. Surv. Subsurface Geol. Series, No. 6 pp. 56-65.

Signor, D. C., and Imes, J. L., 1988, Geohydrology of regional aquifer systems in Cretaceous and older rocks underlying the central U.S.: *in* Swain, L. A., and Johnson, I.A., Regional aquifer systems of the United States, aquifers of the midwestern area, AWRA Monograph Series No. 13.

Sunwall, M. T., Pushkar, P., 1979, The isotopic composition of strontium in brines from petroleum field of southeastern Ohio, Chem. Geol. Vol. 24, pp. 189-197.

Stueber, A. M., Pushkar, P., and Hetherington, E. A., 1987, A strontium isotopic study of formation waters from the Illinois Basin, U.S.A., Appl. Geochemistry, Vol. 2, pp. 477-494.

Walter, L. M., Stueber, A. M., and Huston, T. J., 1990, Br-Cl-Na systematics in Illinois Basin fluids: Constraints on fluid origin and evolution, Geol., Vol. 18, pp. 315-318.

Wilson, T.P., and Long, D. T., 1993, Geochemistry and isotope chemistry of the Michigan basin brines: Devonian formations, Applied Geochemistry, Vol. 8, pp. 81-100.

Worden, R. H, Coleman, M. L., and Matray, J-M, 1999, Basin scale evolution of formation waters: A diagenetic and formation water study of the Triassic

Chaunoy Formation, Paris Basin, Geochimica et Cosmochimica Acta, Vol. 63, No. 17, pp. 2513-2528.

CHAPTER 4:

REGIONAL GEOCHEMICAL AND ISOTOPIC STUDY OF THE GREAT PLAINS AQUIFER SYSTEM (DAKOTA AQUIFER) IN KANSAS, NEBRASKA, AND COLORADO

Abstract

The Great Plains Aquifer system (GP) is one of the largest flow systems in North America, extending from the Artic Circle to New Mexico (Helgeson et al., 1993; Jorgenson et al., 1993). Groundwaters from the GP were collected from Kansas, eastern Colorado and the Nebraska Panhandle from both the unconfined and confined portions of the aquifer. In the study area, two main water types were identified based on their geochemical composition, GP1 and GP2. GP1 is dilute groundwater present in the unconfined portion of the aquifer in Kansas and in confined portion of the aquifer in northeastern Colorado and northwestern Nebraska. GP2 groundwaters are saline groundwaters found in in confined portion of the aquifer in western Kansas and eastern Colorado. The stable isotopic composition of H and O for both GP1 and the GP2 waters suggest that both groundwater types have a meteoric origin. Previous studies of groundwaters similar to GP2 groundwaters suggest that these groundwaters are the product of recharge from the High Plains aquifer system during the most recent North American glaciation. Apparent ages of groundwaters geochemically and geographically similar to GP1 waters in Kansas and GP2 waters in eastern Colorado, suggest that these waters are very old (Clark et al., 1998). The light isotopic signature of this GP1 groundwater suggests that recharge might have occurred at higher elevations and/or during periods of cooler climate.

The analysis of Na-Cl concentrations, Na/Br, and Cl/Br suggest that the salinity of GP2 is due to the dissolution of evaporites. Groundwaters from underlying Permian evaporites could be migrating upwards and mixing with these

groundwaters. Some GP2 groundwaters do not fall along the Meteoric Water Line; this could be due to mixing or to water:rock interaction. The high strontium isotopic signature of a few GP samples could be the result of interaction with shales or k-feldspar within the Cretaceous or Tertiary.

Introduction

The Great Plains Aquifer system (GP), also known as the Dakota aquifer, is comprised of one of the most extensive hydrostratigraphic units of North America (Gosselin et al., 2004, Fig. 4.1). This aquifer system covers 170,000 square miles throughout Kansas, Colorado, Nebraska and adjacent areas (Helgesen and Leonard, 1988). The groundwater in this aquifer ranges from fresh to saline. The dilute groundwater of the GP is used for irrigation and as a source of potable water (Fig. 4.2), but as the population increases in the mid-continent there is going to be an increasing dependence on the water from this aquifer system as a source of potable water (Fig. 4.3). Management of this resource has become an important issue and part of managing this resource is understanding the compositional variability that reflects the complexity of the flow system in the GP (Jorgensen and Signor, 1984). This study will use major ion and H, O, and Sr isotopic tracers to evaluate the processes that may account for the compositional variability in the GP, the presence of different flow systems, the origin of the groundwater, and the source of the salinity in GP groundwater in Kansas, eastern Colorado and the Nebraska Panhandle (Fig.4.4).

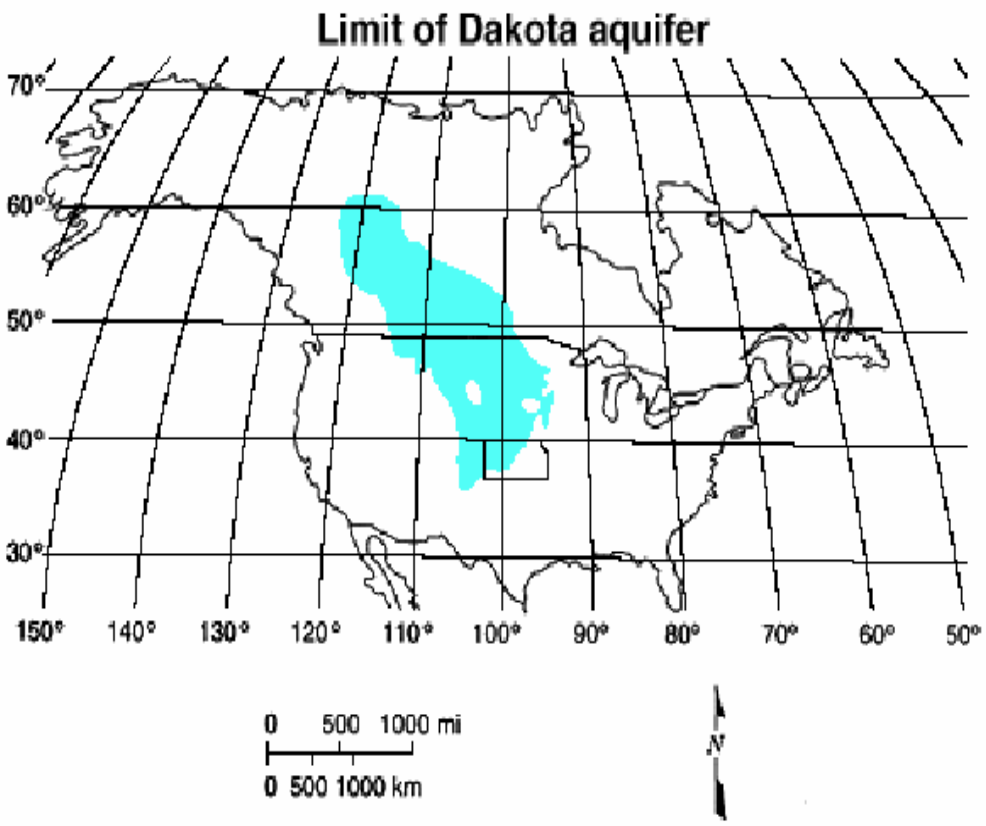


Fig. 4.1 Extent of the Great Plains Aquifer system. From Ground Water Atlas of the United States, Kansas, Missouri, and Nebraska (Miller and Appel, 1997)

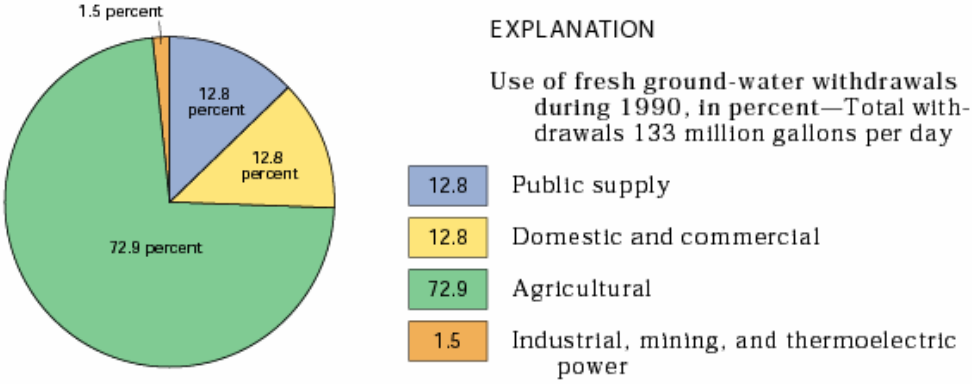


Figure 4.2 Most of the water withdrawn from the aquifer system during 1990 was used for agricultural purposes, primarily irrigation. Data from Miller and Appel, 1997.

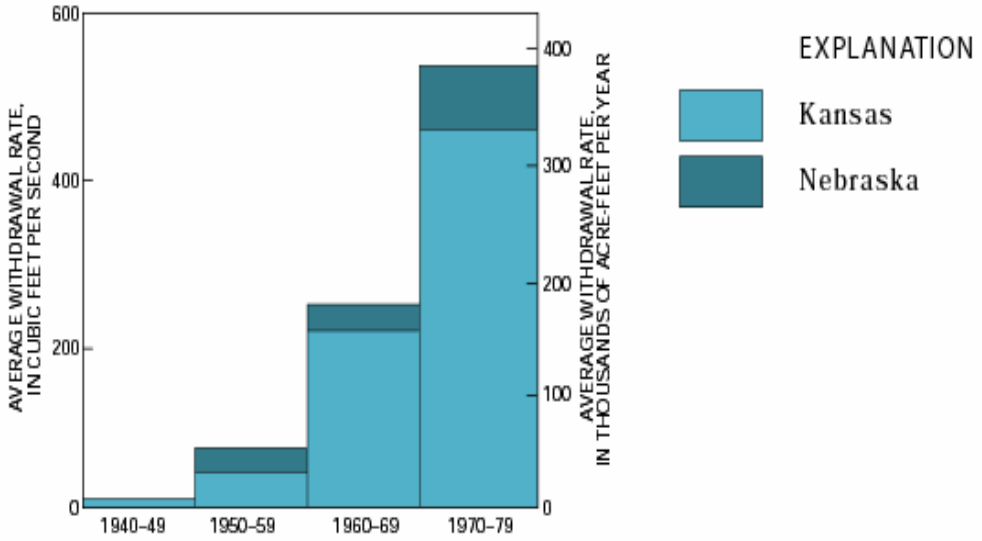


Fig. 4.3 Rates of withdrawal of freshwater from the aquifer system in Kansas and Nebraska increased greatly during the 1960's and the 1970's. Withdrawals in Kansas were much greater than those in Nebraska during these two decades. Figure modified from Helgesen et al. (1993) and Miller and Appel (1997).

Previous work

The Great Plains Aquifer system has been studied extensively since Darton (1905). This author stated that the GP was a classic artesian aquifer. More recent thinking maintains that the GP flow system is far more complex than previously thought (e.g. Jorgensen and Signor, 1984; Clark et al., 1998; Gosselin et al., 2004; Macfarlane et al., 2000). Belitz and Bredehoeft (1988) and Macfarlane (1995) stated that the flow system is influenced by the thickness of the overlying strata and surface drainage basins that down cut into the GP. Although measurements of head and simulations of groundwater flow show that the GP in the eastern part of the study area is not hydraulically connected to the

GP in eastern Kansas (Helgesen et al., 1982; Belitz and Bredehoeft, 1988; Macfarlane, 1995), mixing between the different groundwater types identified suggest otherwise (Clark et al, 1998 and Gosselin et al, 2001).

Based on the H and O stable isotope signature observed in the groundwaters in the GP, previous studies have suggested different recharge scenarios. Dutton (1994), for example, proposed that recharge to this aquifer was through cross-formational flow from the overlying High Plains Aquifer system. According to this model, the groundwater in the High Plains acquired its low isotopic composition due to continental effects and/or high altitude recharge and/or recharge during colder climatic conditions. The continental effect is not sufficient to explain the low isotopic composition of GP groundwater as discussed for WIP groundwater in Chapter 2. The High Plains groundwater subsequently leaked into the GP and was replaced with modern groundwater. Swenson (1968) discusses the idea of recharge to the Dakota Aquifer. According to Swenson (1968), groundwater entered the Mississippian limestones in the Black Hills. Groundwater flowed eastward until the point where the strata between the Mississippian limestones and the Dakota aquifer are absent due to pre-Dakota erosion. In the Black Hills, the water migrates upward from the Mississippian to the Dakota aquifer.

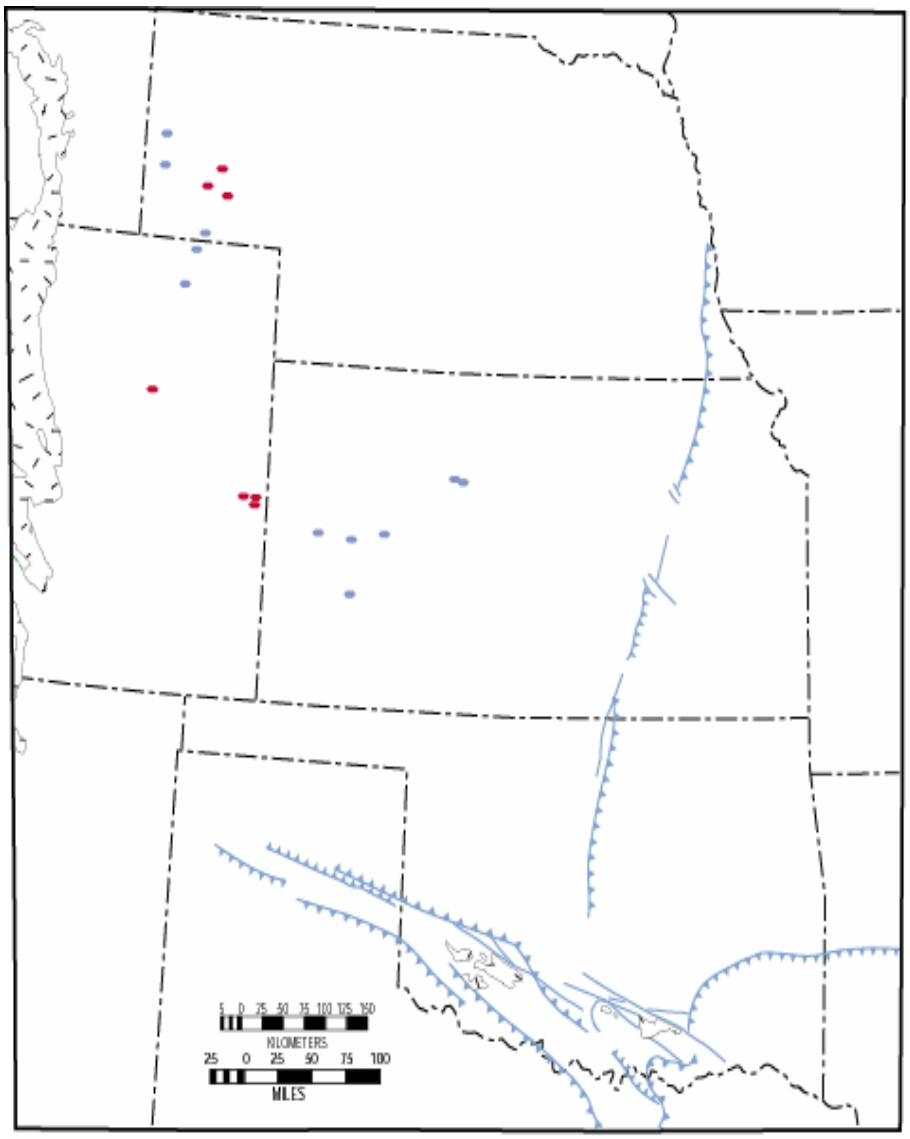


Fig. 4.4 Extent of the study area and sample localities. The GP1 groundwaters are represented by a blue oval while the GP2 groundwaters are represented by a red oval.

Hydrogeologic Setting

The GP lies within the presently tectonically stable interior of the North American craton. Variations in the present day depth to the top of the Precambrian basement show the effects of the Late Cretaceous-Early Tertiary

Laramide orogeny that affected rocks ranging from Paleozoic to Early Tertiary (Helgesen and Leonard, 1988). The GP is structurally controlled by broad basins and arches (Jorgensen et al., 1993). The Dakota Formation is a complex stratigraphic unit of mostly non-marine clastics that were deposited on the margin of the Cretaceous Interior Seaway in western Kansas and eastern Colorado (Macfarlane, et al., 2002). The sand bodies of the Dakota formation are linear to sinuous (Miller and Appel, 1997).

The GP, also known as the Dakota aquifer, overlies the Western Interior Plains confining system (Fig. 4.5). This aquifer system is confined by the Great Plains confining system in eastern Colorado and western Kansas and it becomes unconfined in central Kansas (Fig.4.6). The GP is regionally divided into two sandstone aquifers, the Maha and the Aphishapa, which are separated by a shale confining unit (Miller and Appel, 1997). The upper aquifer is the Maha aquifer and most of the data regarding the GP comes from this aquifer.

In general, groundwater flow in the GP is from west-southwest to east-northeast, with calculated average velocities ranging between 3×10^{-3} m/y to 3 m/y (Helgesen et al., 1993). Porosity ranges between 10% and 30% (Helgeson and Leonard, 1988). Regionally, recharge to this aquifer system occurs in southeast Colorado and northeast New Mexico. Discharge occurs through springs in the Upper Cretaceous in the Nebraska panhandle, to the Arkansas River in central Kansas, and through oil, municipal, and irrigation wells.

Results

GP groundwaters were sampled in eastern Colorado and the Nebraska panhandle. Analytical methods are described in detail in Appendix A. Complete chemical and isotopic results can be found in Appendix B.

Based on Cl concentration and stable isotope variations, the groundwater in the GP can be divided into two groups. GP1 groundwaters are Na-Ca-HCO_3-Cl groundwaters with total dissolved solids ranging between 376 mg/l to 5,600 mg/l (Fig. 4.7 & 4.8). All the samples from Nebraska and northeastern Colorado, the confined portion of the GP, are Na-HCO_3-Cl waters, while the samples in the unconfined portion of the aquifer range from Na-Cl to Na-HCO_3 to Na-Ca-HCO_3 to Na-SO_4 type waters. The samples from Nebraska and northeastern Colorado have the highest TDS for GP1. H and O stable isotope compositions of groundwater samples in this group are very low, with $\delta^{18}O$ values ranging from -13 ‰ to -10 ‰, and δD values ranging from -101 ‰ to –81 ‰. Strontium isotopic compositions (expressed as $^{87}Sr/^{86}Sr$ values) vary from 0.70774 to 0.70938. Group 1 groundwaters are located in Kansas, the Nebraska Panhandle and northeastern Colorado.

GP2 groundwaters are Na-Cl groundwaters, with total dissolved solids ranging between 8,900 mg/l to 130,000 mg/l (Fig. 4.9) The groundwaters from GP2 exhibit a wide range in their stable and radiogenic isotope signatures, with $\delta^{18}O$ values ranging from –11.5‰ to –4.1‰, δD values ranging from –89.8‰ to –55‰, and $^{87}Sr/^{86}Sr$ values varying from 0.70814 to 0.73189.

Discussion

The groundwater geochemical variations encountered in the study area appear to be controlled by the flow system and location within the aquifer, i.e. confined versus unconfined. The complexity of the flow system influences the water quality, with extreme variability between Groups GP1 and the GP2. Data for the GP from Dutton (1994), Gosselin et al. (2001, 2004), and Clark et al. (1998) are compared with data collected in this study.

Major ion chemistry

Based on δD vs. chloride variations, these two groundwater groups do not show any clear mixing trend (Fig. 4.10). The GP1 groundwaters are dilute groundwaters and they are undersaturated with respect to dolomite and calcite, while the GP2 groundwaters are oversaturated with respect to these minerals (Fig. 4.11). Calcium and bicarbonate in these waters may be derived from mixing with fluids migrating upwards from the Pennsylvanian limestones or from fluids migrating downward through the Greenhorn Limestone. The results of groundwater modeling suggest that both GP1 and GP2 groundwaters are oversaturated with respect to k-mica. This suggests that these groundwaters have been in contact with shales that contain micas (Fig. 4.12).

Geohydrologic unit		Principal stratigraphic units	Time-stratigraphic unit
High Plains aquifer		Ogallala Formation and unconsolidated deposits	Quaternary and Tertiary
Great Plains confining system		Pierre Shale, Niobrara Formation, Carlile Shale Greenhorn Limestone, Graneros shale (includes Lower Cretaceous)	Upper Cretaceous
Great Plains aquifer system	Maha aquifer	Dakota Sandstone, "D" sandstone, "J" sandstone, and equivalent Newcastle Sandstone	Lower Cretaceous
	Apishapa confining unit	Kiowa Shale and equivalent of Skull Creek Shale	
	Apishapa aquifer	Cheyenne Sandstone and equivalent of Fall River and Lakota Sandstones	
Western Interior Plains confining system		Shales and Evaporites	Jurassic through Upper Mississippian (Chesterian)

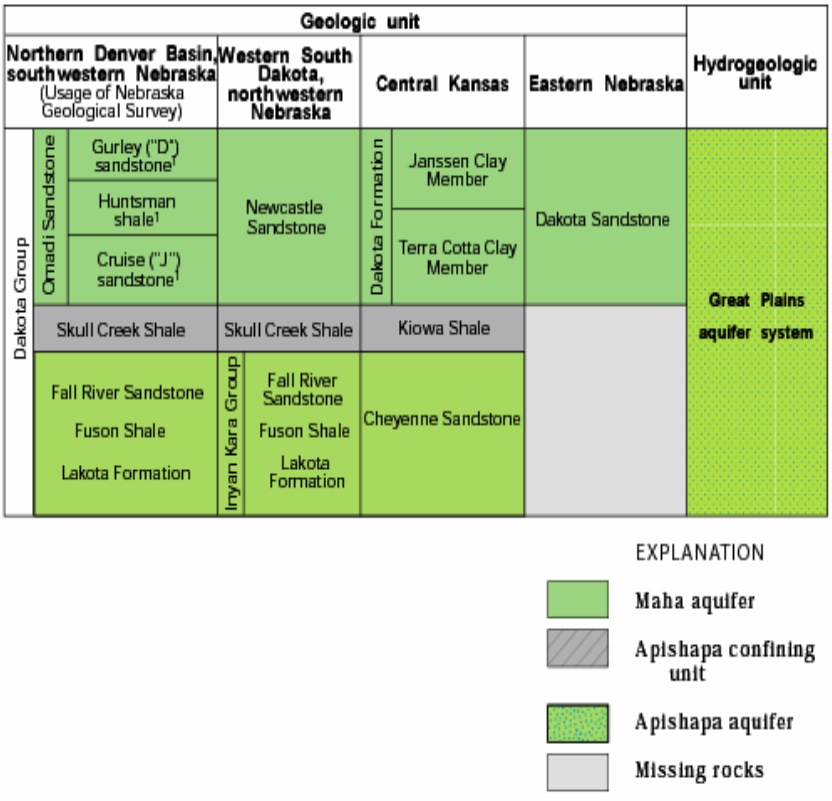


Fig 4.5 General and detailed hydrostratigraphy of the Great Aquifer system for eastern Colorado, Kansas, and Nebraska. Generalized figure was modified from Jorgensen et al. (1993) and detailed hydrostratigaphy figure was modified from Helgesen (1993)

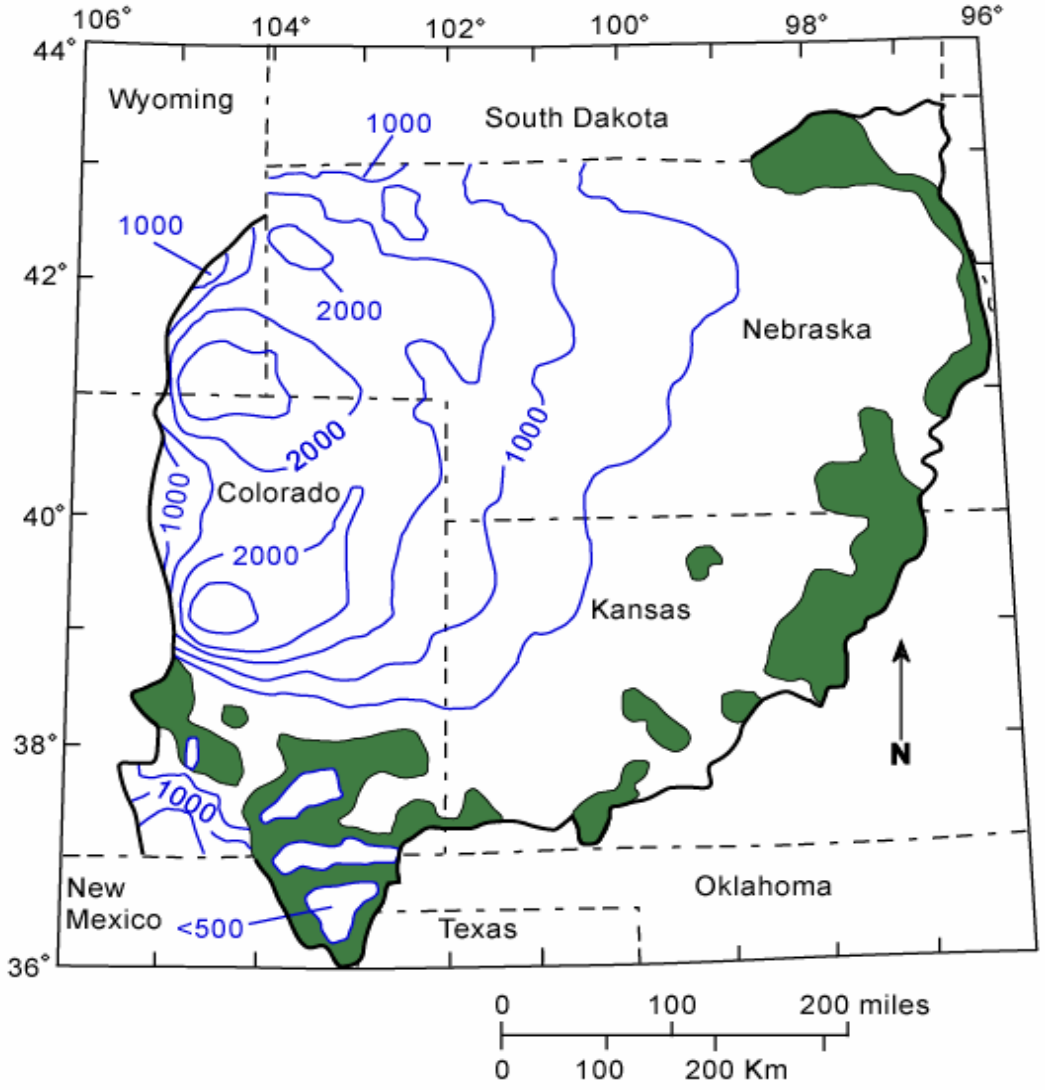


Fig. 4.6 Potentiometric surface map of the Dakota aquifer. The green areas represent the unconfined portion of the aquifer. The blue lines represent lines of equal hydraulic-head difference between the water table and predevelopment potentiometric surface of the Dakota aquifer. The countour interval is 55 feet. Figure was modified from Miller and Appel (1997).

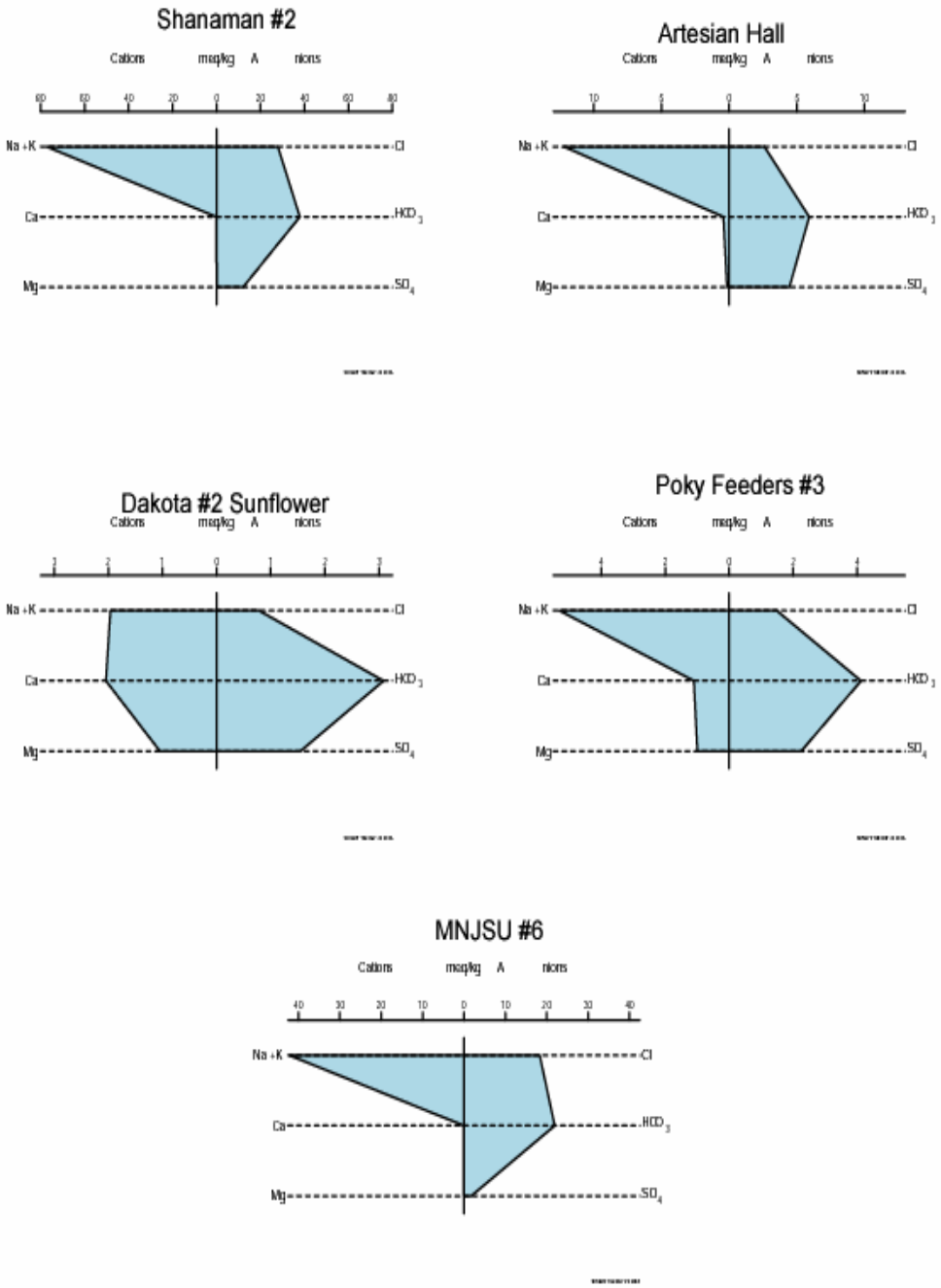


Fig. 4.7 Stiff diagrams of some of the GP1 samples. Modeling was done using the Geochemist's Workbench (Bethke, 1994). It can be seen the samples range from Na-Cl-HCO3 to Na-Ca-HCO3 waters. The Artesian Hall sample is from the Alluvium aquifer in Kansas.

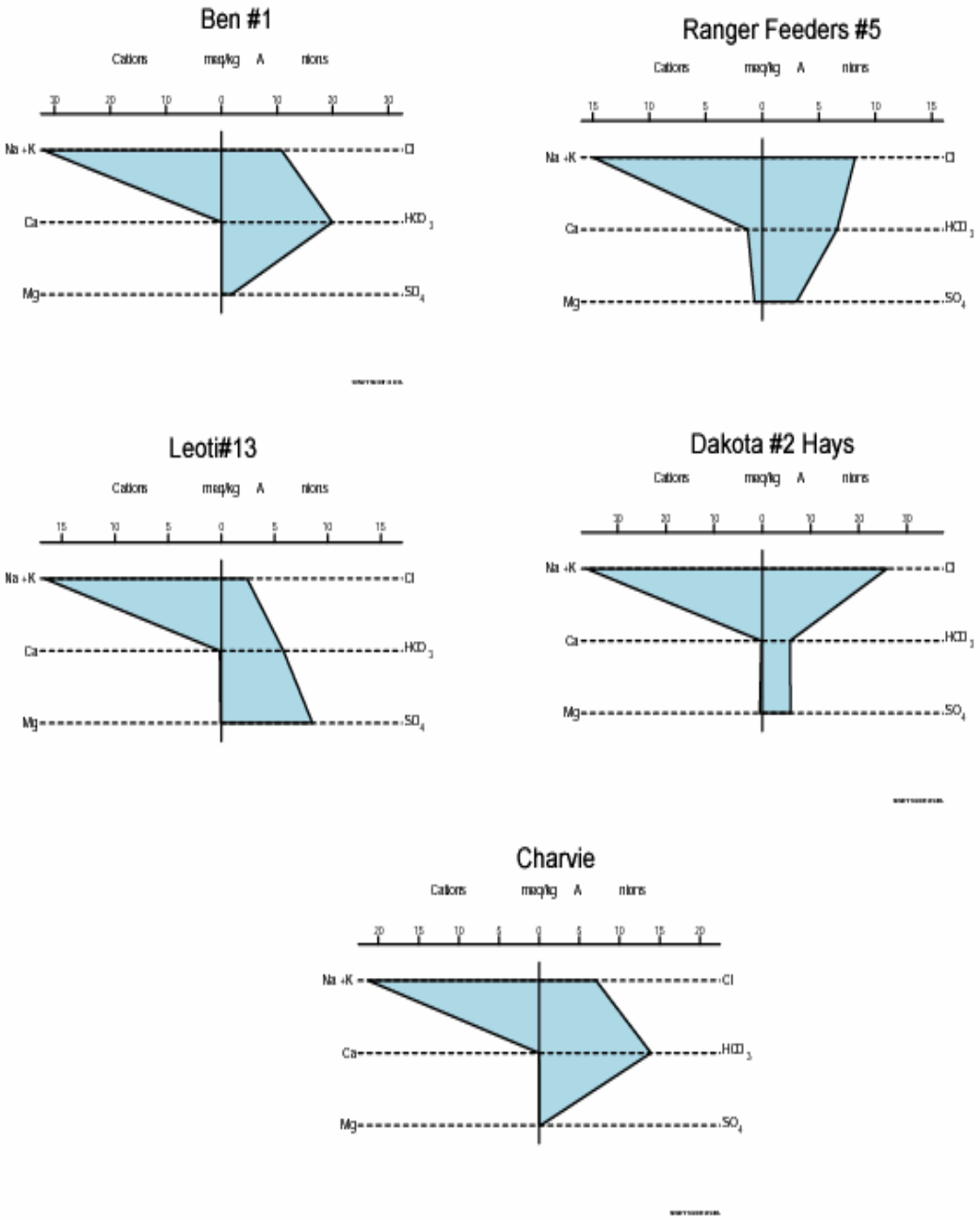


Fig. 4.8 Stiff diagrams of GP1 samples. These groundwaters range from Na-Cl to Na-HCO3 to Na-SO4. Modeling was done using the Geochemist's Workbench (Bethke, 1994) .

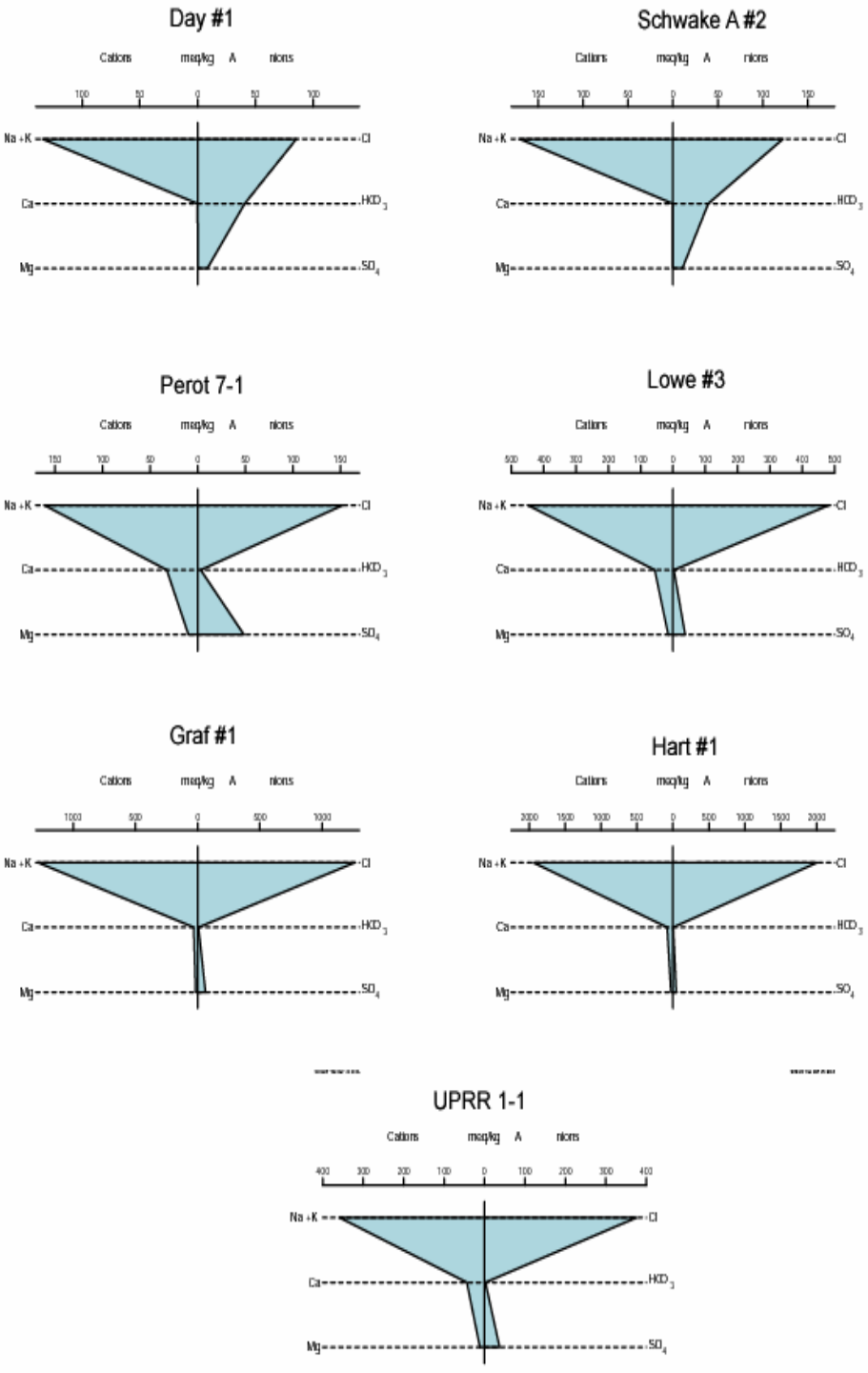


Fig.4.9 Stiff diagrams of GP2 groundwaters. It can be seen that all of these groundwaters are Na-Cl type. Modeling was done using the Geochemist's Workbench (Bethke, 1994)

The high concentrations of Na and Cl in saline groundwater, seawater and evaporite deposits makes these elements, together with Br, good tools for addressing the origin of the salinity in groundwater. Both Cl and Br behave conservatively during seawater evaporation; however Br is preferentially excluded from the halite lattice (Holser, 1979). Br may thus be used to distinguish between salinity models involving the evaporation of seawater or the dissolution of halite. If a saline groundwater acquired its salinity through the

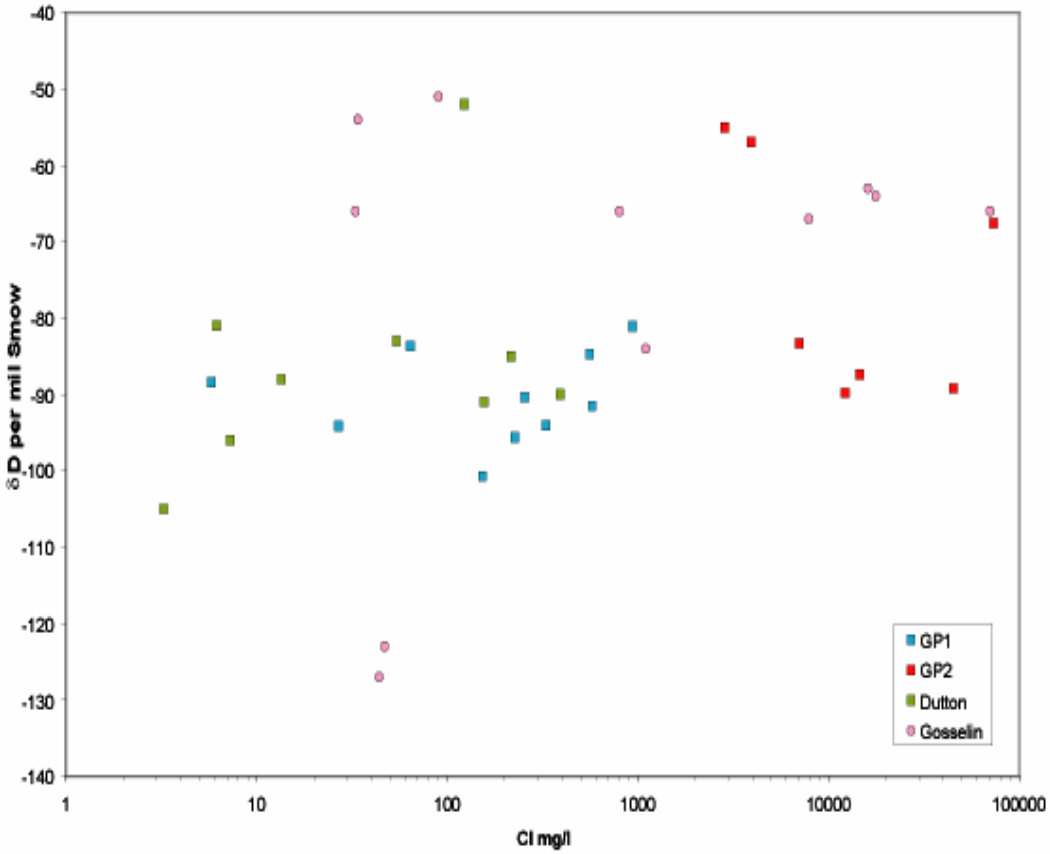


Fig. 4.10 Chloride concentrations and H isotope values for groundwaters in the GP. It can be observed that there is no clear mixing trend between the GP1 waters and the GP 2 waters. Data in this plot is from this study, Dutton (1994) and Gosselin et al. (2001).

evaporation of seawater, Na and Cl are going to be the dominant ions, while Br

concentrations are low relative to those elements. If a saline groundwater acquired its salinity through the evaporation of seawater, Br concentrations should be close to seawater concentrations (Carpenter, 1978). It has been argued that the incongruent dissolution of halite can result in enrichment with respect to Br in the fluid phase (Hanor, 1983; Land and Prezbindowski, 1981).

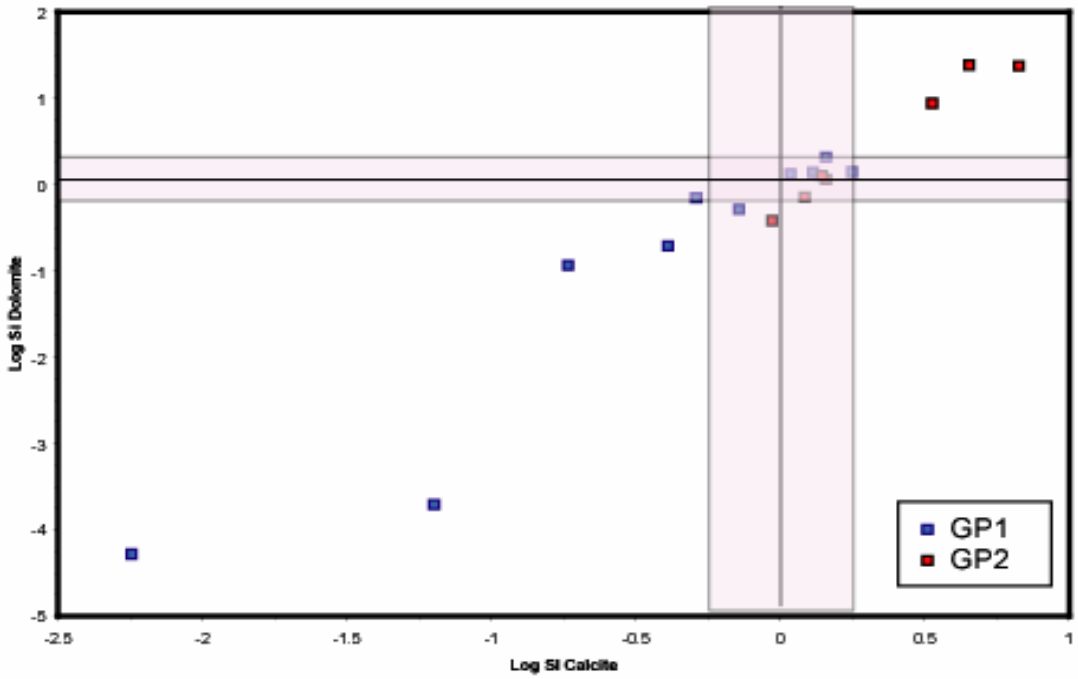


Fig. 4.11 Logarithm of saturation indices (Log S. I.) for calcite and dolomite. Indices were calculated with the thermodynamic equilibrium models PHREEQE (Parkhurst et al., 1980) and PHRQPITZ (Plummer et al., 1988). PHRQPTIZ incorporates Pitzer equations for determination of activity coefficients and it is more accurate with solutions with very high ionic strength, such as GP2 groundwaters. Groundwater samples within the shaded areas are in equilibrium with respect to calcite and dolomite. Most GP2 groundwaters are saturated or oversaturated with respect to calcite while most GP1

Most of the Br and Cl data for GP2 groundwater lie below both seawater and the Br-Cl seawater evaporation trajectory, due to lower Br concentrations ranging

from 6.6 mg/l to 35 mg/l (Fig. 4.13). There are three GP 2 samples that lie along the seawater dilution line. These samples have very high Na and Cl concentrations and Br/Cl rations. These samples could be examples where incongruent dissolution of halite took place. If the groundwater samples are the result of the dissolution of halite, they should lie along the one-to-one line on a

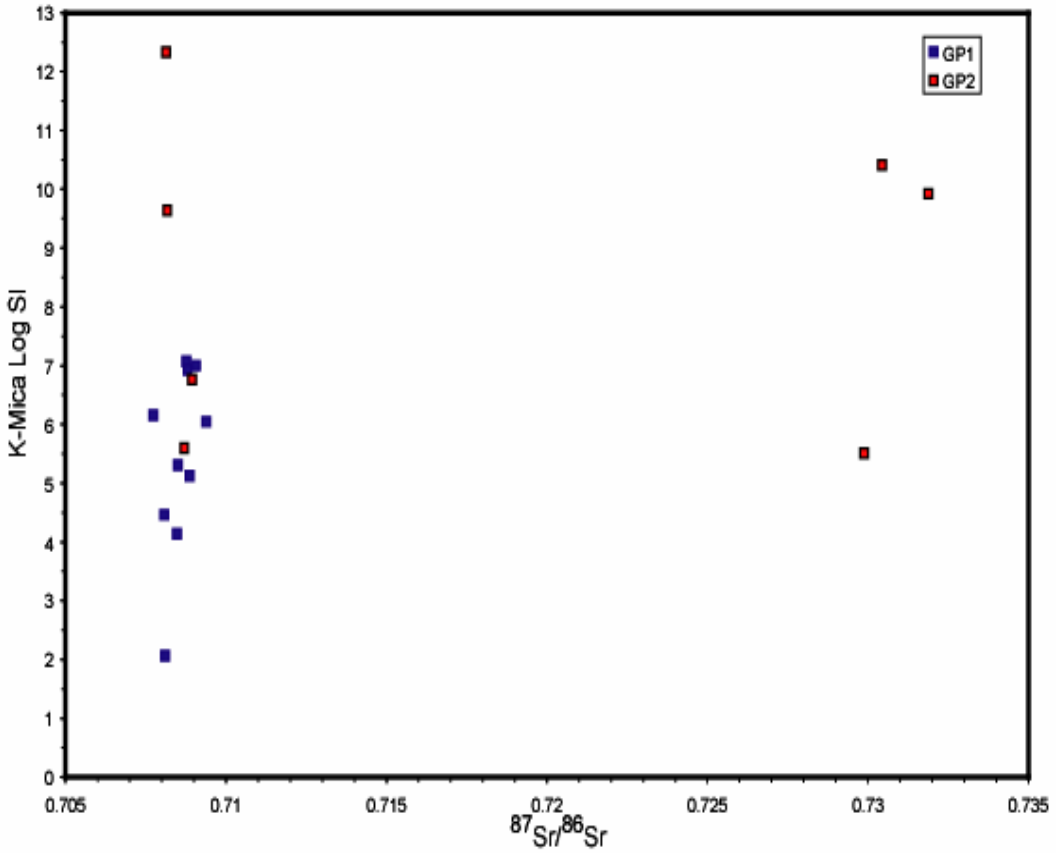


Fig. 4.12 Degree of saturation and strontium isotopic composition for GP1 and GP2 groundwaters. It can be seen that all the samples are oversaturated with respect to potassium mica, however oversaturation with respect to k-mica does not correlate to high strontium isotopic values. This could indicate that the k-mica is not the source for the high strontium isotopic values observed in the study area.

Na-Cl plot (Fig. 4.14). All of the GP2 samples lie along that one-to-one line, suggesting that the salinity of the GP2 groundwater resulted from the dissolution of halite.

Gogel (1981) documents modern-day processes of dissolution of Permian evaporites in central Kansas, in particular the dissolution of the Hutchison Salt Member in the Wellington Formation. There are two main sources of evaporites in the mid-continent, the Hutchison Salt Member of the Wellington Formation and the Nipewalla Group. Both evaporites are Permian in age. A more detailed description of the Nipewalla Group is provided in Chapter 3. Dissolution of either of these evaporite units would require upwards, cross-formational flow to account for the salinity of GP groundwater. Bredehoeft et al., (1983) stated that since development most of the groundwater released is from storage in the confining units. This would suggest that saline groundwater from the confining system would mix with the GP groundwater.

H and O isotopes

Most of the GP1 and GP2 samples fall along the Meteoric Water Line, suggesting that they are meteoric in origin (Fig. 4.15). With a few exceptions both GP1 and GP2 exhibit a very light isotopic signature. Three different mechanisms have been proposed for the origin of these groundwaters; 1) recharge at high altitude along the Colorado Front Range, 2) local recharge occurring only during the winter months, or 3) local recharge of precipitation

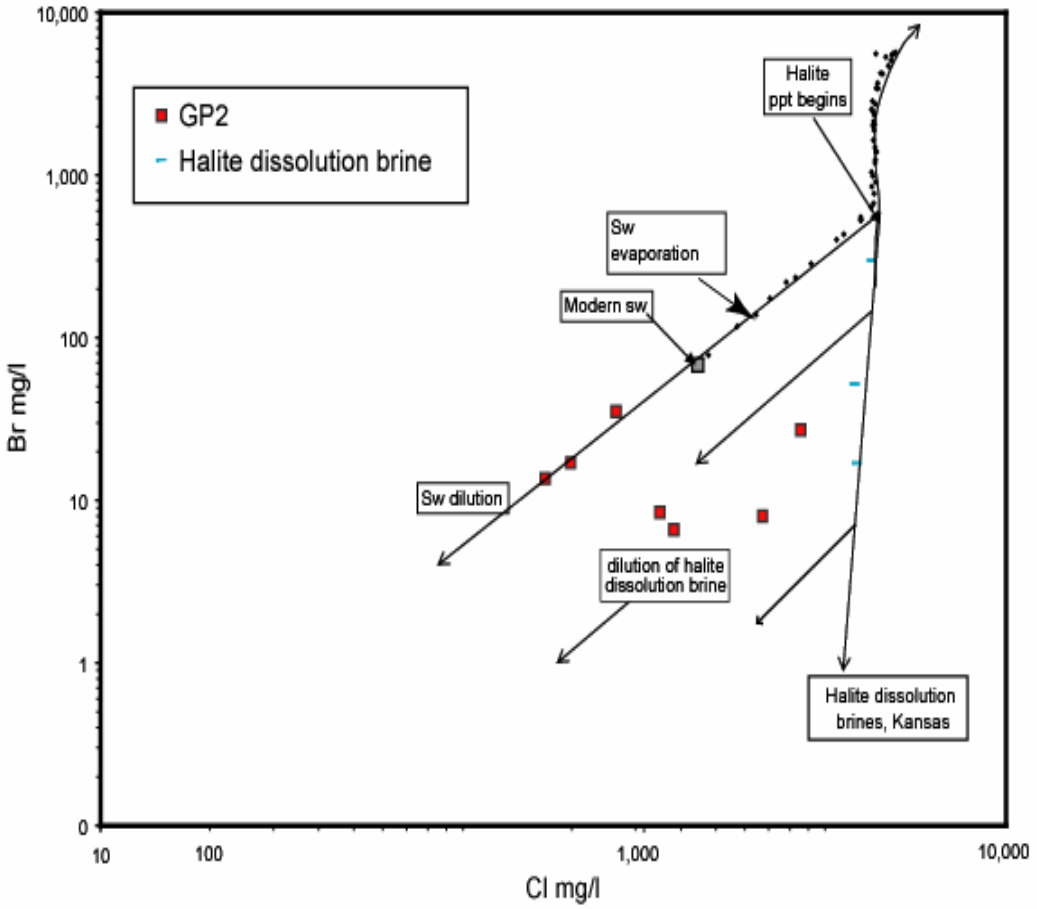


Fig. 4.13 Bromide and chloride concentrations for GP2 groundwaters relative to seawater evaporation trajectory. Most of the GP2 samples fall along the halite dissolution and the dilution of halite dissolution brines. Three data points fall along the seawater dilution trend. This could be due to the incongruent dissolution of halite, causing an enrichement on Br concentrations. Halite dissolution brine is from Gogel (1981), seawater evaporation data is from McCaffrey et al. (1987).

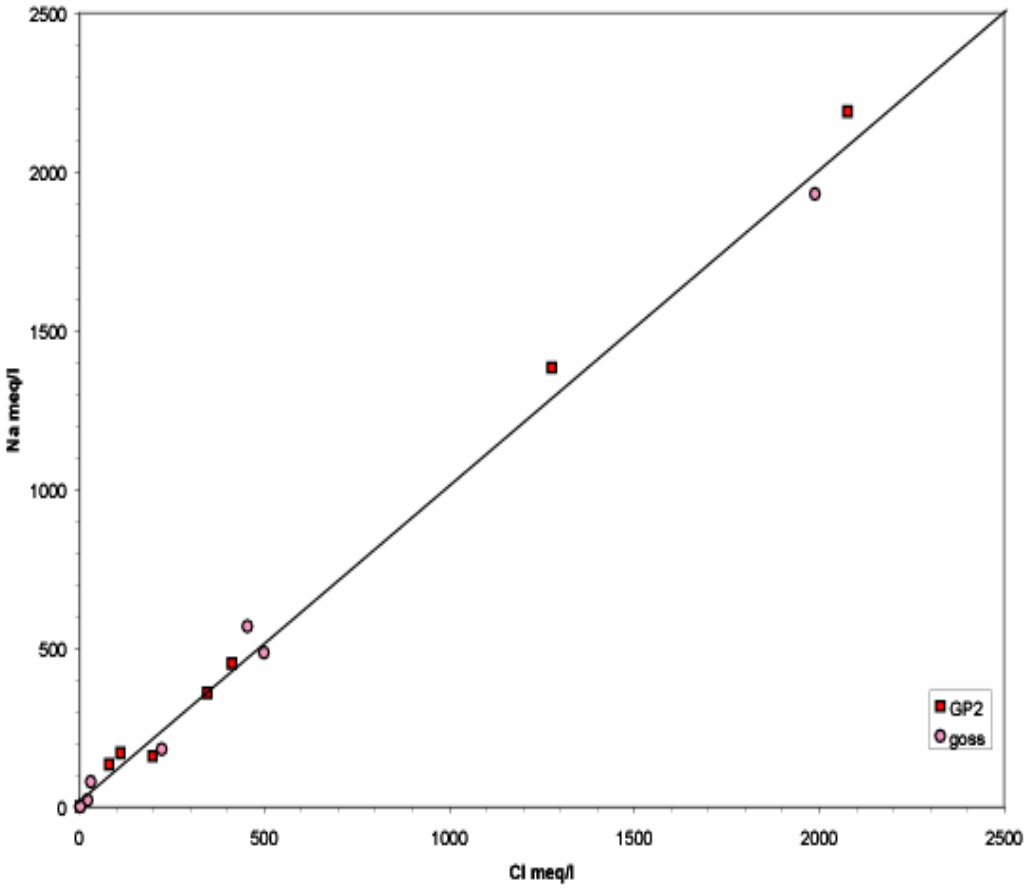


Fig. 4.14 Plot of Na vs Cl in meq/l. All the data falls close to the one-to-one line suggesting that the salinity for GP2 originated from the dissolution of evaporites.

under cooler climatic conditions and/or glacial meltwater during the Pleistocene (Rostron and Holmden, 2000).

Clark et al. (1998) concluded, based on noble gas data and ^{14}C, which groundwaters in western Kansas had apparent ages of about 20,000 yrs. GP1 in Kansas and GP2 in western Colorado are similar to those groundwaters described by Clark et al. (1998). These groundwaters have very small range in O isotopic values of -12‰ to-11.‰. The apparent ages for these groundwaters suggest that recharge occurred prior to Last Glacial Maximum, during a period of

intermediate climate (20 to >50 kyr ago) (Clark et al., 1998) (Fig. 4.15). These groundwaters probably recharged at higher elevations in the Colorado Front Range and are part of a regional scale flow system.

GP1 samples in northeastern Colorado and the Nebraska Panhandle have a very small range in $\delta^{18}O$, from -13‰ to -10‰ (Fig. 4.15). The oxygen isotope values for GP2 groundwaters for the same area range between -10‰ to -4‰ (Fig. 4.15). Dutton (1995) stated that the groundwaters in the Nebraska panhandle could have recharged either by migration down from the High Plains aquifer system, or through recharged on aquifer outcrop areas or due to continental effects. Based on ^{14}C measurements, he calculated apparent groundwater ages between 15,000 yrs to 35,000 yrs. The light isotopic signature of the GP1 groundwaters suggests that these groundwaters recharged at either high altitude or during colder climatic conditions, or both. The O isotopic composition for the GP2 groundwaters in this area could have been affected by mixing with waters infiltrating from the Western Interior Plains aquifer system.

Strontium Isotopes

The strontium isotopic compositions of GP1 and GP2 groundwaters are very low, with the exception of three samples, Lowe #3, UPRR 1-1, and Perot 7-1, in the GP2 Group (Fig. 4.16). The strontium isotopic composition for those

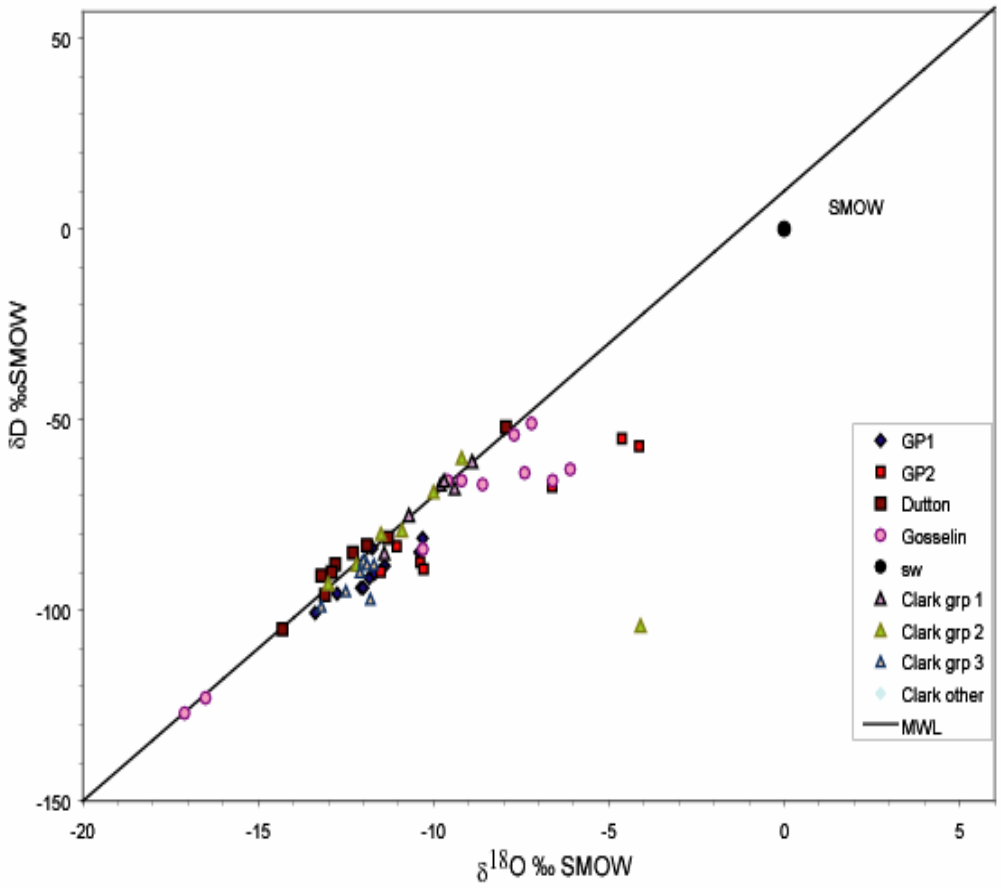


Fig. 4.15 Plot of hydrogen vs oxygen stable isotopes. Most of the samples fall along the MWL suggesting that this samples have meteoric origin. A few samles are to the right of the MWL, this could be due to water:rock interaction or fluid mixing proceses. GP data in this plot are from this study, Dutton (1994), Gosselin et al. (2001), and Clark et al. (1998)

groundwater samples range between 0.729888 and 0.731891. Those three samples are from the Sorrento field in Cheyenne County, Colorado. Chaudhuri et al. (1987) sampled groundwaters from the Morrow sandstone from the same field, and these waters have strontium isotope values ranging between 0.71834 to 0.71947. Chaudhuri et al. (1987) inferred that these groundwaters acquired

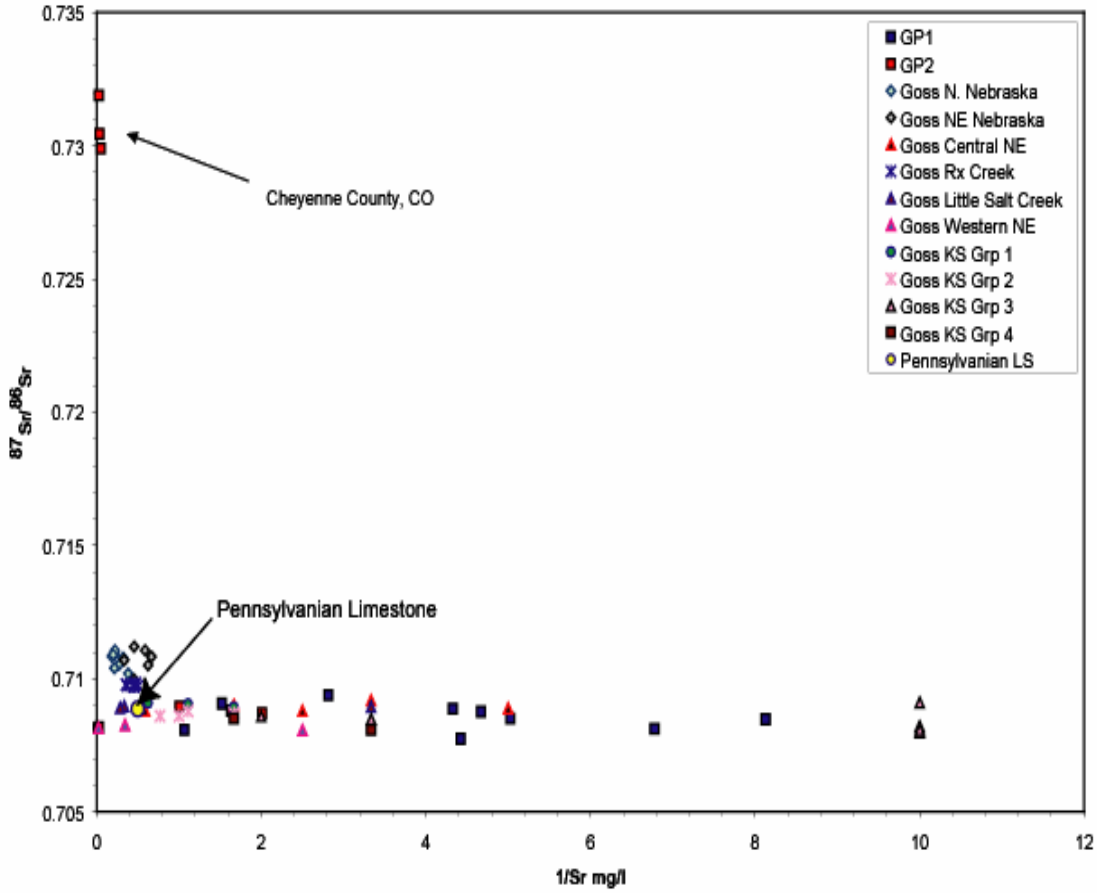


Fig. 4.16 Strontium isotope and strontium isotope concentration variations in the GP groundwaters and host Pennsylvanian limestone. Most of the samples fall within a relatively narrow range with the exception of the samples from Cheyenne County and the samples from northern and northeastern Nebraska. The remainder of the samples have a strontium isotopic signature simiar to that of the Pennsylvanian Limestone in the mid-continent.

their high isotopic signature through interaction with the Precambrian basement along the Central Kansas Uplift. However, these samples are closer to the Las Animas Arc, where the Morrow formation is not juxtaposed with the Precambrian basement.

Sonnenberg et al. (1991) determined that the secondary porosity observed in the Morrow sandstone was due to the dissolution of feldspars and

lithic grains. These authors does not state if the feldspars are k-feldspar or plagioclase.

Mass balance modeling of rock:water interaction processes was undertaken to constrain the extents of interaction involved. The modeling follows that outlined in Banner et al. (1989) and Musgrove and Banner (2004). Rock:water interaction modeling between clay and Lowe #3, UPRR 1-1, and Perot 7-1 was done. Rock:water interaction modeling between these three groundwaters and clays suggest that it takes very little interaction before the groundwaters equilibrate to the strontium isotopic signature of the clay (Fig. 3.18). As discussed in Chapter 2, the most probable processes by which these groundwaters acquired their high strontium isotopic composition are the dissolution and replacement of detrital alkali feldspars and micas and the illitization of smectite (Chaudhuri and Clauer, 1993). Chaudhuri and Clauer (1993) argued that the albitization of plagioclase is one of the main processes by which groundwaters can acquire a high strontium isotopic composition. During this process K-feldspar is replaced by other minerals such as calcite or anhydrite, which in turn is replaced by albite.

Conclusions

Groundwater in the Great Plains aquifer can be divided into different geochemical Groups, GP1 and GP2. O and H isotope values for GP1

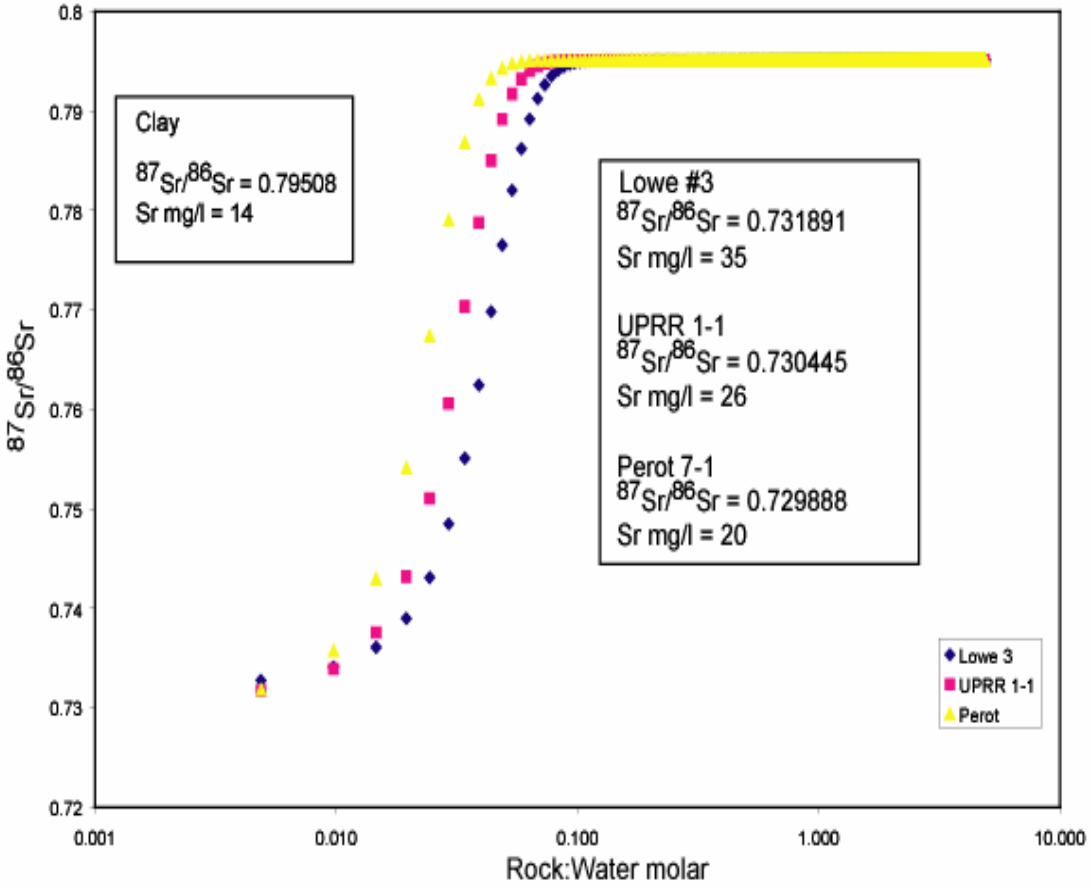


Fig. 4.17 Results of water:rock interaction modeling between the Cheyenne County groundwater samples and mid-continent shales. The groundwater equilibrates with the rock before a rock:water ratio of 1. These waters were interacted with clays. Clay data is from Gilleti and Casserly (1994).

groundwater samples in Kansas and eastern Colorado suggest, together with tracer data and ^{14}C ages from previous studies (Clark et al., 1998, Dutton, 1995, Macfarlane et al., 2000), that these groundwaters are old and probably recharged at higher elevations in the Colorado Front Range. GP1 and GP2 samples in northern Colorado and the Nebraska Panhandle probably recharged at high altitude and/or during colder climatic conditions.

The GP2 salinity developed through mixing with fluids that have been in contact with Permian evaporites within the Western Interior Plains aquifer system. These high salinity waters are only found in the confined portion of the aquifer.

Most of the groundwaters in the GP have strontium isotopic signatures similar to Pennsylvanian limestone. Three water samples, from the same hydrocarbon field, have high strontium isotopic signatures. The high strontium values could be the result of interaction with shales that contain K-feldspar. The most probable processes by which these groundwaters acquired their high strontium isotopic composition are the dissolution and replacement of detrital alkali feldspars and micas and the illitization of smectite.

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References

Banner, J. L., Wasserburg, G. J., Dobson, P. F., Carpenter, A. B., and Moore, C. H., 1989, Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri, Geochimica and Cosmochimica Acta, Vol. 53, pp. 383-398.

Belitz, K., and Bredehoeft, J. D., 1988, Hydrodynamics of the Denver Basin: Explanation to Subnormal Fluid Pressures, AAPG, Vol. 72, No. 11, pp. 1334-1359.

Bethke, C. M, 1994, The Geochemist Workbench, version 2.0, A Users Guide to Rxn, Act2, Tact, React, and Gtplot, Hydrogeology Program, University of Illinois.

Bredehoeft, J. D., Neuzil, C. E., and Milly, P. C. D., 1983, Regional flow in the Dakota aquifer, a study of the role of confining layers, USGS Water Supply paper No. 2237, 45 p.

Carpenter, A. B., 1978, Origin and chemical evolution of brines in sedimentary basins, Oklahoma Geological Survey Circular 79, pp. 60-70.

Chaudhuri, S., Broedel, V., and Clauer, N., 1978, Strontium isotopic composition of oil-field waters from carbonate reservoir rocks in Bindley field, central Kansas, U.S.A., Geochimica et Cosmochimica Acta, Vol. 51, pp. 45-53.

Chaudhuri, S., and Clauer, N., 1993, Strontium isotopic compositions and potassium and rubidium contents of formation waters in sedimentary basins: Clues to the origin of the solutes, Geochimica et Cosmochimica Acta, Vol. 57, pp. 429-437.

Clark, J. F., Davisson, M. L., Hudson, G. B., and Macfarlane, P. A., 1998, Noble Gases, Stable Isotopes and Radiocarbon as Tracers of Flow in the Dakota Aquifer, Colorado and Kansas, Journal of Hydrology, Vol. 211, pp. 151-167.

Darton, N. H., 1905, Preliminary report on the geology and underground water resources of the central Great Plains, USGS Professional Paper, 433 p.

Dutton, A. R., 1994, Sources and ages of ground water in unconfined and confined aquifers beneath the U.S. high plains, Final technical report, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas.

Dutton, A. R., 1995, Groundwater Evidence for Paleorecharge in U.S. High Plains Aquifers, Quaternary Research, Vol. 43, pp. 221-231.

Epstein, S., and Mayeda, T.K., 1953, Variations of O^{18} contents of waters from natural sources, Geochimica and Cosmochimica Acta, Vol. 4, pp. 213-224.

Giletti, B J., and Casserly, J. E. D., 1994, Strontium diffusion kinetics in plagioclase feldspars, Geochimica et Cosmochimica Acta, Vol. 58, Issue 18, pp. 3785-3793.

Gogel, T., 1981, Discharge of saltwater from Permian rocks to major stream-aquifer systems in central Kansas, Kansas Geological Survey, Chemical Quality Series No. 9, 60 p.

Gosselin, D., Harvey, F. E., and Frost, C. D., 2001, Geochemical Evolution of Ground Water in the Great Plains (Dakota) Aquifer of Nebraska: Implications for the Management of a Regional Aquifer system, Ground Water, Vol. 39, No. 1, pp. 98-108.

Gosselin, D. C., Harvey, E. F., Forst, C. D., Stotler, R. and Macfarlane, P. A., 2004, Strontium Isotope Geochemistry of Groundwater in the Central part of the Dakota (Great Plains) Aquifer, USA, Applied Geochemistry, Vol. 19, pp. 359-377.
Hanor, J. S., 1987, Origin and migration of subsurface sedimentary brines, SEPM Short Course No. 21, 247 p.

Hanor, J. S., 1983, Fifty years of development of thought on the origin and evolution of subsurface sedimentary brines: *in* Boardman, S. J. (ed.), Revolution in the Earth Sciences, Kendal Hunt Publishing Co., pp. 99-111.

Helgesen, J. O., and Leonard, R. B., 1988, Geohydrology of the Great Plains aquifer system, central United States *in:* Swain, L. A, and Johnson, A. I., (eds.), 1988, Regional Aquifer systems of the United States, Aquifers of the Midwestern area, AWRA Monograph series No. 13, pp. 179-190.

Helgesen, J. O., Leonard, R. B., and Wolf, R. U., 1993, Hydrology of the Great Plains Aquifer System in Nebraska, Colorado, Kansas, and adjacent areas, USGS Professional Paper, 1414-E.

Holdoway, K. A., 1978, Deposition of evaporites and red beds of the Nipewalla Group, Permian, western Kansas, Kansas Geol. Survey Bull., No. 215, 43p.

Holser, W. T., 1979, Mineralogy of evaporites *in*: Burns, R. G. (ed.), 1979, Mineralogical Society of America short course notes, Vol. 6, pp. 211-294.

Jorgensen, D. G., Helgesen J. O., and Imes, J. L., 1993, Regional aquifers in Kansas, Nebraska, and parts of Arkansas, Colorado, Missouri, New Mexico, Oklahoma, south Dakota, Texas and Wyoming-geohydrologic framework, USGS Professional Paper 1414-B.

Jorgensen, D. G, and Signor, D. C., (eds.), 1984, Geohydrology of the Dakota aquifer, Proceedings of the First C. V. Theis conference on geohydrology; geohydrology of the Dakota aquifer. Lincoln, NE, Oct. 5-6, 1982, 247 p.

Knauth, L. P. and Beeunas, M. A., 1986, Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters, Geochimica et Cosmochimica Acta, Vol. 50, pp. 419-433.

Land, L. S., and Prezbindowski, D, R., 1981, The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A., Journal of Hydrology, Vol. 54, pp. 51-74.

Macfarlane, P. A., 1995, The effect of river valleys and the Upper Cretaceous aquitard on regional flow in the Dakota aquifer in the central Great Plains of Kansas and southeastern Colorado, Kansas Geological Survey Bulletin, Vol. 238, pp. 11-30.

Macfarlane, P. A., Clark, J. F., Davisson, M. L., Hudson, G. B., and Whittemore, D. O., 2000, Late-Quaternary Recharge Determined from Chloride in Shallow Groundwater in the Central Great Plains, Quaternary Research, Vol. 53, pp. 167-174.

Macfarlane, P. A., Förster, A, Merriam, D. F., Schrötter, J., and Healy, J. M., 2002, Monitoring Artificially Stimulated Fluid Movement in the Cretaceous Dakota Aquifer, Western Kansas, Hydrogeology Journal, Vol. 10, pp. 662-673.

McCaffrey, M. A., Lazar, B., and Holland, H. D., 1987, The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite, Journal of Sedimentary Petrology, Vol. 57, No. 5, pp. 928-937.

Miller, J. E. and Appel, C. L., 1997, Groundwater Atlas of the United States, Kansas, Missouri, and Nebraska, USGS HA 730 D.

Musgrove, M., and Banner, J. L., 2004, Controls on the spatial and temporal variability of vadose dripwater geochemistry; Edwards Aquifer, central Texas, Geochimica et Cosmochimica Acta, Vol. 68, Issue 5, pp. 1007-1020.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE; a computer program for geochemical calculations, Water Resources Investigations, USGS, WRI 80-96, 216 p. s

Plummer, L. N., Prestemon, E. C., and Parkhurst, D. L., 1991, An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, USGS Water Resources Investigation Report 91-4078, 227 p.

Swenson, F. A., 1968, New theory of recharge to the artesian basin of the Dakotas, GSA Bulletin, Vol. 79, Issue 2, pp. 163-182.

CHAPTER 5
SUMMARY AND CONCLUSIONS

Three distinct groundwater types are identified in the Western Interior Plains aquifer system (WIP) in the mid-continent, each originating in different geographic locations. The pontentiometric surface map, the mixing patterns of these groups and their geographical extent suggest that the WIP is hydraulically connected through out the mid-continent. Based on mass-balance model results, fluid mixing exerts a significant control over the geochemical and isotopic character of the three different groundwater groups present in the WIP. Water:rock interaction has altered the strontium isotopic signature of Groups 2 and 3, suggesting that fluids have been in contact with Pennsylvanian shales, Precambrian basement, or argillaceous components within the carbonate aquifer unit. Two different mechanisms for generating saline fluids were recognized in the WIP: dissolution of evaporites and evaporation of seawater.

Two different water types are recognized in the Great Plains aquifer system (GP). The light isotopic signature in the GP suggests that these groundwaters could have recharged at high altitude during colder climatic conditions. The salinity in the GP groundwater is the result of this groundwater mixing with fluids that have been in contact with the Permian evaporites. There are a few samples in eastern Colorado that exhibit a very high strontium isotopic composition, which could be the result of interaction with Pennsylvanian shales or shales from the GP confining system.

This study determined that the WIP is a hydraulically connected system in the mid-continent. Even though there is still uncertainty over the existence of regional-scale flow systems, the WIP in the mid-continent USA can be used as a

modern analog to investigate ancient regional scale flow systems and to understand processes that control hydrocarbon migration, diagenesis of deeply buried sandstones and limestones, and ore fluid generation. This finding can also impact the possibility of using this aquifer system as a repository for hazardous waste material or greenhouse gases.

It was also determined that groundwater mixing exerts a fundamental control on the groundwater geochemical and isotopic composition over a regional scale. Water:rock interaction has further evolved the geochemical composition of the groundwater. Due to the scale of this flow system, water:rock interaction processes could have affected the geochemical composition of the water depending on the geographic location and structural style.

The GP also constitutes a regional scale flow system that is recharged by different sources according geographic location. Central Kansas and eastern Colorado groundwaters were recharged in the Colorado Front Range at high altitude while in western Nebraska and northeastern Colorado the groundwaters were recharged at high altitude along with colder climatic conditions.

The geochemical and isotopic character of the GP groundwater was influenced by saline fluids migrating from the Permian evaporites. Water:rock interaction was found to affect a few GP groundwater samples in eastern Colorado. The high strontium isotopic signature could be due with interaction with shales.

The approach to tracing hydraulic continuity and groundwater evolution in regional scale flow systems differs from studies on local scales that use

introduced tracers such as dyes. To evaluate the origin and evolution of groundwater in a regional scale system a variety of geochemical and isotopic tools are employed. Chloride and H and O isotopes are suitable for tracing fluid mixing processes. Na, Cl, Br, Ca relationships were used to evaluate the origin of the saline fluids. Strontium isotopes together with K/Rb ratios were used to ascertain the extent of water:rock interaction. H and O isotopes can be used to determine the origin of the groundwater and to suggest processes that might be affecting the groundwater composition, such as water:rock interaction or mixing.

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Appendix A

Sampling and Analytical Methods

A. Sampling

During August 1996 and October 1998 groundwater samples from water, oil, and gas wells were collected from Cambrian to Cretaceous units. Sampling criteria consisted of collecting waters from untreated wells that were not flooded or screened or open to more than one formation. Treated wells were injected with corrosion inhibitors, scaling inhibitors, and de-emulsifiers. One sample, Ray A # 4, was collected from the well before treatment and after treatment and no significant difference was noted in their chemical and isotopic analysis results (Tables B1-B6). As a precaution, however, treated wells were avoided for groundwater sampling. The level of production of some of the oil fields in Kansas, Colorado, and Oklahoma has decreased through time due to continuous pumping, so in order to increase the efficiency of recovery, the older oil wells are flooded with carbon dioxide, open to more than one formation, or re-injected with water. Wells open to more than one formation are common in northwest Kansas. Since one of the goals of this study is to assess the extent of vertical migration of groundwater, wells that are open to more than one formation were not useful. Additionally, since sometimes the formations are not the same lithology it becomes increasingly difficult to constrain the evolution of water chemistry. CO_2 injection changes the chemistry of the groundwater, so wells that were flooded with carbon dioxide were not useful to this study. In some wells the saline groundwaters are disposed of by re-injecting them into the formation. The re-

injection of saline groundwaters alters the chemistry of the groundwater in the formation and thus makes this kind of well unsuitable for sampling.

All groundwaters were collected in acid-cleaned one-gallon containers where the water and the oil were allowed to separate. After separation, a Teflon tube was inserted into the water section of the sample. Samples were filtered through a stack of three filters (0.45μ, 1.2μ, and 5μ) attached to a syringe. The one-gallon containers used for collection were not reused. VOA vials were precleaned with soap solution and deionized water and then used to collect filtered samples for hydrogen and oxygen isotope analysis. Containers used for the collection of groundwater for cation analysis and strontium isotopic analysis were acid cleaned, while containers used for the collection of groundwater for anion analyses were cleaned with soap solution and deionized water. Additionally, one-gallon containers, syringes, Teflon tubes, and filters were acid cleaned.

B. Analytical methods

1. H and O isotopes

I conducted the hydrogen and oxygen analyses at Southern Methodist University's Stable Isotope Laboratory, with the assistance of Dr. Kurt Ferguson. The oxygen isotopic composition of the groundwaters was determined using a method similar to that described by Epstein and Mayeda (1953). Two to five millimeters of sample was equilibrated for 24 hours with CO_2 gas of known carbon isotopic composition. The equilibrated CO_2 gas was cryogenically

purified and loaded into a sample tube. At least one in-house laboratory standard was analyzed with each set of unknown samples. Analytical reproducibility for δD and $\delta^{18}O$ based on replicates of water samples and standards for this study were $\pm$ 1.0 and $\pm$ 0.1, respectively.

All oxygen isotope replicate analyses in Tables 19 and 20 were equilibrated for 24 hours, the same as the procedure for all samples, with the exception of Rathjen #1, Regier #1 A and Straily. The replicates for these three highly saline samples were allowed to equilibrate for 36 hours in order to address possible analytical artifacts resulting from the increased time required for saline waters to reach oxygen isotope equilibrium between CO_2 gas and water (Horita, 1989). The time required to achieve equilibrium is particularly high for $MgCl_2$ and $CaCl_2$ brines because there is a sharp decrease in solubility of CO_2 in these salt solutions, which results in lower $\delta^{18}O$ values for shorter equilibration times (Horita, 1989). For two of the three saline samples, the different equilibration times yielded deviations of 0.08 and 0.35 per mil, which are similar to the mean deviation of 0.09 for the other replicate analyses in the data set (Tables B19 and B20). The Rathjen #1 sample yielded a larger deviation of 0.7 per mil, with a lower $\delta^{18}O$ value for the 36 hour equilibration time. This difference is in the opposite direction from that predicted by Horita's (1989) experimental results. In summary, the replicate analyses indicate that the saline nature of the WIP groundwaters has not significantly affected the results of the analytical procedures.

The hydrogen isotopic composition of the saline groundwaters was determined using a method similar to that described by Bigeleisen et al. (1952). Five microliters of cryogenically purified water was reduced to H_2 gas by passing it over depleted uranium metal at 800 °C. The H_2 gas was then collected onto activated carbon at liquid nitrogen temperatures. At least one in-house standard was analyzed with each set of groundwaters. Five percent of the samples were analyzed twice. All isotopic measurements for oxygen and hydrogen were made on a Finnigan MAT 251 mass spectrometer.

2. Strontium Isotopes

Strontium isotope analyses were determined using a Finnigan-MAT 261 thermal ionization mass spectrometer (TIMS) at the University of Texas at Austin, with the assistance of Dr. Larry Mack**.** Water samples for strontium isotope analyses were aliquoted to Teflon vials and then evaporated to dryness on a hotplate. Samples were redissolved in 330 μL of 0.3 M ultrapure HNO_3 for ion exchange chemistry. Sr was separated via ion exchange chemistry using Teflon micro-columns, Eichrome Industries Inc. Sr Specific resin (fine), ultrapure HNO_3 and Nanopure deionized water. Approximately 200 ng Sr were loaded on to Ta filaments in a HNO_3 and H_3PO_4 medium. Analyses were performed in dynamic multicollection mode and corrected offline for fractionation using an in-house correction based on an empirical relationship between instrument fractionation and $^{87}Sr/^{86}Sr$ value (Housh and McMahon, 2000). In order to assess the analytical reproducibility of an individual strontium isotope analysis, I compiled analyses of the SRM 987 Sr standard that were conducted in the TIMS

laboratory by its multiple users during the course of this study. Thirty-two analyses of this standard yielded a mean value of 0.710262, and two standard deviations of the population of 0.000016. The mean deviation of replicate analyses of unknowns in this study (Table B.19 in Appendix B) is lower than this value, indicating that this is a conservative estimate of the analytical reproducibility. Laboratory processing blank for strontium was 10 picograms.

3. Cations and Anions

Cation samples were analyzed at the University of Minnesota on a Perkin Elmer/Sciex ELAN 5000 ICP-MS. The samples were diluted with 0.2 N HCL in an amount appropriate to bring the element concentrations within the calibrated limits of the standard. In general, the samples were diluted to 1000 mg/l TDS. Anion samples were analyzed at the University of Minnesota on a Dionex ion chromatography system consisting of a GP40 pump module, a CD20 conductivity detector and an AS4A anion separator columns in tandem. The eluant is carbonate/bi-carbonate based. The samples were diluted with deionzied water to a TDS of 1000 mg/l. Groundwater samples from the first field season in 1996 were first analyzed for cation and anions at the University of Texas at Austin on a JY ICP OES and a single column ion chromatograph, respectively. The detection limits for cations and anions ranged between 0.005 and 0.015. Due to significant charge balance errors (10 to 20%) these samples were re-analyzed at the University of Minnesota for anions. The newer anion results reduced the charge balance error of these samples to below 5%, likely as a result of the improved backgrounds and complex matrix capabilities of tandem column IC.

Sixty four percent of the water samples analyzed for this dissertation have charge balance errors of less than 5%, while the remaining 36% of the samples have a charge balance error between 5% and 10%. The majority of the 5-10% samples have salinities ranging from 40,000 mg/l to 100,000 mg/l. Such increases in charge balance error in saline fluids could be due to uncertainties associated with the measurement of sulphate concentrations such as precipitation of sulphate salts prior to analysis (Taylor et al., 1996), or to the necessity of performing multiple dilutions for elemental analysis of saline waters (Gascoyne, 2004). These charge balance errors, although not below the 5% level indicative of a high-quality analysis, do not affect the interpretations and conclusions presented in this dissertation.

Bicarbonate was measured in the field by titrating groundwater samples to a pH of 4.5. The pH of each sample was measured as soon as it was collected and filtered. Approximately 50 mls of sample was put in a beaker together with a Teflon stirring bar. HCl acid was added in small increments of approximately 0.05 mls using a Gilmont microburette, measuring the pH of the sample after each addition until a pH of about 5 was reached. At this point, the titrating acid was added dropwise until a pH of 4.5 was obtained.

Field blanks were collected using deionized water at six different localities in western-central Kansas, eastern Oklahoma, the Nebraska panhandle, and eastern Colorado. Field blanks were filtered into bottles identical to those used for sample collection. The majority of cation and anion results for blanks were below detection limit (0.005 to 0.01 mg/l). The blank-to-sample ratios are

negligible for the samples analyzed. Silica was found in all six blanks with concentrations ranging from 0.04 to 0.44 mg/l. Potassium was also found in three of the field blanks with concentrations ranging from 0.07mg to 0.09 mg/l. Finally, calcium was measured in three field blanks, ranging from 0.1 to 0.9 mg/l. For most of the samples analyzed, the silica, potassium, and calcium blanks do not introduce uncertainties larger than the analytical uncertainty, and no blank corrections were applied to the data reported. The results for the blanks and replicates are provided in Appendix B. Thirty three percent of the samples were run in replicate, for both cation and anion analysis, with a precision better than ± 3%. Charge balance errors were determined by NETPATH and PHREEQC, while saturation indices were calculated using PHREEQPTZ. Charge balance information and saturation indices are provided in Appendix B.

Appendix B

GP and WIP Geochemical and Isotopic data

Table B.1 Location, formation, and age for the WIP

Well name	Group	County/State	Formation	Age
Groening # 1	2B	Marion, KS	Viola	WIP/ORD
Fernback J #1	2B	Texas, OK	Krider	
Cooley #4	2B	Graham Co., KS	Kansas City	WIP/PEN
Cooley #1	2B	Graham Co., KS	Kansas City	WIP/PEN
Shear "A"	2B	Ness Co., KS	Mississippian	WIP/MISS
Von Lintel #2	2B	Ellis Co., KS	Arbuckle	WIP/CAMB
Miller #4	2B	Rooks Co., KS	Arbuckle	WIP/CAMB
UPRC 1-35	2B	Cheyenne Co., CO	Arbuckle	WIP/CAMB
Kriley E2	2C	Rooks, KS	Arbuckle	WIP/CAMB
George West	2C	Rooks, KS	Penn.conglomerate	WIP/PENN
Schmalzried	2C	Ness, KS	Mississippian	WIP/MISS
Wiltrout #1	2C	Norton Co., KS	Kansas City	WIP/PEN
Warren #1	2C	Phillips Co., KS	Kansas City	WIP/PEN
Holley #201	2C	Graham Co., KS	Kansas City	WIP/PEN
Ray "A" #4	2C	Rooks Co., KS	Arbuckle	WIP/CAMB
Ray "A" #4*	2C	Rooks Co., KS	Arbuckle	WIP/CAMB
Hart # 1 LSE	3B	McPherson, KS	Mississippian	WIP/MISS
Roland Ratzloff #1	3B	Marion, KS	Mississippian	WIP/MISS
Kulhmeier #1	3B	McPherson, KS	Mississippian	WIP/MISS
Morrison #1	3B	Saline, KS	Mississippian	WIP/MISS
Van Meter # 1	3B	Saline, KS	Mississippian	WIP/MISS
Orland Unrue #2	3B	McPherson, KS	Hunton	WIP/DEV-ORD
Regier # 1 (A)	3C	Harvey, KS	Kansas City	WIP/PENN
Kriley G2	3C	Rooks, KS	Kansas City	WIP/PENN
Boles F - 1	3C	Seward, KS	St. Louis Limestone	WIP/MISS
Franze E-1	3C	Beaver, OK	Kansas City	WIP/PENN
James O'Dea A-1	3C	Stevens, KS	Chester	WIP/MISS
Charles 1-12	3C	Haskell, KS	Morrow	WIP/PENN
Hanke A-1	3C	Seward, KS	Morrow	WIP/PENN
USA No. AD-2	3C	Morton, KS	Morrow	WIP/PENN
Mowrey W.H. #1	3C	Texas, OK	Krider	WIP/PENN
Rathjen #1	3C	Texas, OK	Krider	WIP/PENN
Straily	3C	Ellis Co., KS	Kansas City/Lansing	WIP/PEN

Ray “A” #4* is the sample collected after the well was treated for scaling, corrosion and and emulsifiers.

Table B.2 Well depth, pH, Temperature, Eh, and conductivity for the WIP

Well name	Group	Well depth	pH	T C	Eh	Conductivity ms/cm
Groening # 1	2B	1,000	6.87	27	-305.3	67
Fernback J #1	2B	844	7.33	22.3	-150.4	38.3
Cooley #4	2B	NA	6.7	35.6	-271	64.7
Cooley #1	2B	NA	6.53	35.2	-303	30.1
Shear "A"	2B	NA	6.65	33.3	-277	47.2
Von Lintel #2	2B	NA	6.36	34.5	-276	71.5
Miller #4	2B	NA	6.4	27.9	-292	54
UPRC 1-35	2B	NA	7.89	38.8	-406	49.2
Kriley E2	2C	1,097	6.73	25.2	-247.5	92
George West	2C	NA	6.31	21.1	-292	93.1
Schmalzried	2C	NA	6.51	22.1	-271.3	66.1
Wiltrout #1	2C	NA	7.04	31.6	-258	85.4
Warren #1	2C	NA	7	35	-179	88.9
Holley #201	2C	NA	6.8	29.2	-323	88.7
Ray "A" #4	2C	NA	6.78	28.9	-309	83.9
Ray "A" #4*	2C	NA	6.77	28.8	-309	84.78
Hart # 1 LSE	3B	818	6.5	23.2	-199.6	121.2
Roland Ratzloff #1	3B	893	6.8	17.6	-184.2	118.8
Kulhmeier #1	3B	916	7.04	20.4	-50.6	125.4
Morrison #1	3B	875	6.7	25.1	-158.5	124.8
Van Meter # 1	3B	NA	6.78	24.2	-312.8	128.3
Orland Unrue #2	3B	1,023	7.07	20.8	-275.8	130.1
Regier # 1 (A)	3C	869	6.05	25.3	-226.0	>199.9
Kriley G2	3C	1,067	6.85	18.2	-46	169.4
Boles F - 1	3C		6.48	22.8	-12.8	144
Franze E-1	3C	2,057	6.51	25.2		155.4
James O'Dea A-1	3C	1,703	6.65	18	-70	134.2
Charles 1-12	3C	1,628	6.56	22	-30	151.8
Hanke A-1	3C	1,639	6.52	23.5	-19.7	152.1
USA No. AD-2	3C	1,673	6.14	22.8	-45.5	151
Mowrey W.H. #1	3C	831	6.96	22.7	-137.5	162.3
Rathjen #1	3C	797	6.92	22.9	-140	164
Straily	3C	NA	6.6	27.8	-151	191.2

Table B.3 Geochemical data for the WIP

Well name	Group	TDS mg/l	Cl mg/l	SO_4 mg/l	Br mg/l	NO_3 mg/l	HCO_3 mg/l
Groening # 1	2B	45,333	26,569	1,788	80	<0.005	244
Fernback J #1	2B	27,053	12,220	5,024	4	13	195
Cooley #4	2B	45,436	24,508	1,804	53	<0.005	313
Cooley #1	2B	20,047	8,999	1,834	8	<0.005	1,708
Shear "A"	2B	30,288	15,792	1,963	24	<0.005	412
Von Lintel #2	2B	50,399	26,861	2,124	50	<0.005	464
Miller #4	2B	35,937	19,860	1,891	36	<0.005	678
UPRC 1-35	2B	35,710	15,055	3,947	6	<0.005	3,684
Kriley E2	2C	64,324	39,120	2,780	112	<0.005	225
George West	2C	65,514	39,490	1,474	103	<0.005	41
Schmalzried	2C	49,921	29,338	2,938	101	<0.005	469
Wiltrout #1	2C	61,986	34,031	2,138	36	<0.005	259
Warren #1	2C	64,715	35,450	1,863	31	<0.005	122
Holley #201	2C	63,642	34,886	707	10	<0.005	805
Ray "A" #4	2C	58,822	31,674	1,902	25	<0.005	330
Ray "A" #4*	2C	60,302	32,061	1,902	NA*	NA*	329
Hart # 1 LSE	3B	84,827	53,391	176	187	<0.005	98
Roland Ratzloff #1	3B	83,926	54,782	137	151	<0.005	122
Kulhmeier #1	3B	88,968	56,220	138	166	<0.005	106
Morrison #1	3B	95,184	61,134	1,316	176	<0.005	128
Van Meter # 1	3B	94,041	60,194	862	173	<0.005	204
Orland Unrue #2	3B	90,988	55,591	1,390	201	<0.005	222
Regier # 1 (A)	3C	188,270	117,015	393	581	<0.005	56
Kriley G2	3C	135,785	89,244	212	240	<0.005	138
Boles F - 1	3C	160,169	100,307	1,080	181	<0.005	37
Franze E-1	3C	216,789	136,992	740	170	<0.005	42
James O'Dea A-1	3C	128,417	80,541	824	152	<0.005	101
Charles 1-12	3C	185,957	117,437	592	266	<0.005	72
Hanke A-1	3C	190,016	119,486	602	298	<0.005	127
USA No. AD-2	3C	181,503	112,895	414	461	<0.005	80
Mowrey W.H. #1	3C	246,524	155,526	2,532	117	<0.005	44
Rathjen #1	3C	238,719	149,284	2,576	56	<0.005	42
Straily	3C	176,105	102,248	1,631	45	<0.005	60

Table B.4 Geochemical data for the WIP

Well name	Group	Li mg/l	B mg/l	Na mg/l	Mg mg/l	Al mg/l	Si mg/l
Groening # 1	2B	3.48	6.51	14,170	576	0.01	1.16
Fernback J #1	2B	1.14	4.14	8,984	213	0.00	7.41
Cooley #4	2B	16.84	<0.005	15,640	561	0.03	7.28
Cooley #1	2B	7.96	<0.005	6,530	380	0.03	8.63
Shear "A"	2B	15.06	<0.005	9,912	400	0.03	9.20
Von Lintel #2	2B	22.22	<0.005	17,280	621	0.06	6.04
Miller #4	2B	15.53	<0.005	10,908	527	0.06	8.97
UPRC 1-35	2B	11.07	<0.005	12,102	218	1.20	11.40
Kriley E2	2C	3.46	15.36	19,260	570	0.03	17.30
George West	2C	9.97	13.93	20,640	886	0.04	11.14
Schmalzried	2C	10.43	18.48	14,130	601	0.04	15.80
Wiltrout #1	2C	16.24	<0.005	22,614	460	0.06	5.73
Warren #1	2C	12.00	<0.005	24,096	466	0.06	5.83
Holley #201	2C	15.55	<0.005	25,722	341	0.06	18.39
Ray "A" #4	2C	17.29	<0.005	21,846	453	0.06	5.88
Ray "A" #4*	2C	12.00	<0.005	23,388	467	0.06	6.21
Hart # 1 LSE	3B	5.23	9.30	26,820	978	0.04	2.82
Roland Ratzloff #1	3B	4.72	12.34	25,660	673	0.03	13.57
Kulhmeier #1	3B	5.25	10.67	28,570	830	0.03	4.46
Morrison #1	3B	6.58	12.65	27,370	1,086	0.02	22.41
Van Meter # 1	3B	4.46	10.22	27,860	1,146	0.08	13.35
Orland Unrue #2	3B	7.34	9.31	28,500	1,024	0.06	5.99
Regier # 1 (A)	3C	4.92	10.41	56,120	2,994	0.28	0.00
Kriley G2	3C	5.03	9.43	38,560	1,890	0.07	13.96
Boles F - 1	3C	14.56	19.85	47,540	1,658	0.05	22.15
Franze E-1	3C	7.61	10.77	67,320	2,108	0.12	0.00
James O'Dea A-1	3C	13.72	12.72	36,350	1,633	0.35	4.35
Charles 1-12	3C	4.28	18.90	54,120	2,427	0.39	0.00
Hanke A-1	3C	3.44	10.10	55,790	2,201	0.10	0.00
USA No. AD-2	3C	5.20	11.37	49,760	2,173	0.11	16.86
Mowrey W.H. #1	3C	6.84	6.93	79,480	1,821	0.03	4.08
Rathjen #1	3C	8.51	3.47	81,390	1,257	0.07	5.35
Straily	3C	37.76	<0.005	65,056	1,288	0.06	3.81

Table B.5 Geochemical data for the WIP

Well name	Group	P mg/l	K mg/l	Ca mg/l	Fe mg/l	Mn mg/l	Rb mg/l
Groening # 1	2B	<0.005	109	1,789	0.38	0.49	0.12
Fernback J #1	2B	0.07	35	350	10.92	0.89	0.04
Cooley #4	2B	<0.005	300	2,218	0.01	0.04	<0.005
Cooley #1	2B	<0.005	115	441	0.01	0.01	<0.005
Shear "A"	2B	<0.005	265	1,474	0.01	0.02	<0.005
Von Lintel #2	2B	<0.005	345	2,608	0.06	0.03	<0.005
Miller #4	2B	<0.005	290	1,699	0.10	0.10	<0.005
UPRC 1-35	2B	<0.005	340	322	0.20	0.20	<0.005
Kriley E2	2C	0.53	144	2,113	0.21	0.15	0.21
George West	2C	0.59	220	2,584	0.28	0.05	0.27
Schmalzried	2C	0.00	266	2,073	0.31	0.10	0.75
Wiltrout #1	2C	<0.005	340	2,062	0.01	0.17	<0.005
Warren #1	2C	<0.005	260	2,366	0.35	0.40	<0.005
Holley #201	2C	<0.005	430	650	0.04	0.01	<0.005
Ray "A" #4	2C	<0.005	565	1,962	0.10	0.10	<0.005
Ray "A" #4*	2C	<0.005	60	2,008	0.10	0.10	<0.005
Hart # 1 LSE	3B	<0.005	148	2,939	3.06	0.13	0.15
Roland Ratzloff #1	3B	<0.005	130	2,207	4.52	0.13	0.15
Kulhmeier #1	3B	<0.005	153	2,702	1.23	0.13	0.18
Morrison #1	3B	0.10	189	3,774	1.94	0.18	0.24
Van Meter # 1	3B	0.63	122	3,313	0.55	0.13	0.13
Orland Unrue #2	3B	<0.005	177	3,829	0.31	0.56	0.21
Regier # 1 (A)	3C	<0.005	197	9,814	0.80	0.09	0.32
Kriley G2	3C	0.92	225	5,170	32.49	0.44	0.23
Boles F - 1	3C	<0.005	631	8,538	7.91	0.14	1.40
Franze E-1	3C	<0.005	517	8,635	1.43	0.08	0.59
James O'Dea A-1	3C	<0.005	400	8,205	28.67	0.88	0.74
Charles 1-12	3C	<0.005	471	10,330	0.48	0.24	0.52
Hanke A-1	3C	<0.005	363	10,800	72.15	4.99	0.48
USA No. AD-2	3C	<0.005	168	14,560	75.64	8.20	0.43
Mowrey W.H. #1	3C	0.05	461	6,481	7.13	0.28	0.38
Rathjen #1	3C	0.15	368	3,692	4.65	0.12	0.30
Straily	3C	<0.005	895	4,708	1.99	0.10	<0.005

Table B.6 Geochemical and isotopic data for the WIP

Well name	Group	Sr mg/l	Ba mg/	Pb mg/	Charge Balance	$\delta^{18}O$	δD
Groening # 1	2B	75	0.68	<0.01	2.0	-11	-89
Fernback J #1	2B	7	0.04	0.01	3.0	-9	-62
Cooley #4	2B	66	0.12	0.61	-7.7	-8	-76
Cooley #1	2B	23	0.08	0.44	-3.3	-10	-77
Shear "A"	2B	45	0.10	0.69	-5.2	-10	-79
Von Lintel #2	2B	65	0.14	1.54	-7.7	-9	-77
Miller #4	2B	54	0.11	2.80	-0.2	-8	-74
UPRC 1-35	2B	14	0.20	2.00	-0.3	-7	-83
Kriley E2	2C	74	0.10	0.01	7.6	-6	-67
George West	2C	141	1.74	<0.01	2.1	-8	-69
Schmalzried	2C	61	0.10	0.01	6.8	-8	-65
Wiltrout #1	2C	59	0.13	0.91	-5.9	-4	-59
Warren #1	2C	71	0.19	0.97	-7.7	-4	-54
Holley #201	2C	66	0.32	0.35	-8.0	-7	-67
Ray "A" #4	2C	61	0.16	2.98	-8.1	-4	-56
Ray "A" #4*	2C	63	0.13	2.51	-10.3	NA	NA
Hart # 1 LSE	3B	240	16.23	0.01	3.7	-4	-45
Roland Ratzloff #1	3B	167	12.25	0.01	9.0	-3	-42
Kulhmeier #1	3B	220	6.22	<0.01	4.3	-4	-42
Morrison #1	3B	142	0.66	0.02	8.4	-7	-64
Van Meter # 1	3B	275	35.25	0.01	7.3	-4	-46
Orland Unrue #2	3B	232	0.43	<0.01	2.3	-5	-56
Regier # 1 (A)	3C	1658	5.39	<0.01	1.4	2	-17
Kriley G2	3C	280	3.84	0.01	9.0	-3	-45
Boles F - 1	3C	310	1.74	0.02	3.5	-3	-34
Franze E-1	3C	414	0.20	<0.01	4.3	1	-25
James O'Dea A-1	3C	301	1.46	<0.01	3.2	-3	-36
Charles 1-12	3C	482	0.73	0.01	3.6	1	-26
Hanke A-1	3C	554	2.32	<0.01	3.2	1	-21
USA No. AD-2	3C	1329	7.24	0.02	1.3	1	-18
Mowrey W.H. #1	3C	153	0.08	0.01	-5.9	-1	-27
Rathjen #1	3C	87	0.18	0.01	5.2	-2	-29
Straily	3C	156	0.45	5.31	-4.6	0.29	-37

Table B.7 Strontium isotope values and saturation indices for the WIP

Well name	Group	$^{87}Sr/^{86}Sr$	Calcite log IAP/KT	Dolomite log IAP/KT	Gypsum log IAP/KT
Groening # 1	2B	0.711141+-8	0.39	0.73	-0.22
Fernback J #1	2B	0.709087+-8	NA	NA	NA
Cooley #4	2B	0.71026+-7	0.50	0.92	-0.17
Cooley #1	2B	0.71821+-7	0.46	1.31	-0.61
Shear "A"	2B	0.72476+-7	0.41	0.73	-0.19
Von Lintel #2	2B	0.72095+-8	0.38	0.64	-0.06
Miller #4	2B	NA	0.36	0.63	-0.17
UPRC 1-35	2B	0.70898+-8	1.88	4.08	-0.60
Kriley E2	2C	0.713288+-8	0.25	0.35	0.00
George West	2C	0.71303+-7	0.48	0.87	-0.21
Schmalzried	2C	0.71860+-9	0.29	0.43	0.06
Wiltrout #1	2C	0.71586+-7	0.68	1.20	-0.15
Warren #1	2C	0.72372+-7	0.41	0.64	-0.17
Holley #201	2C	0.71095+-6	0.45	1.10	-1.10
Ray "A" #4	2C	0.71571+-11	0.48	0.79	-0.21
Ray "A" #4*	2C	NA	NA	NA	NA
Hart # 1 LSE	3B	0.709209+-8	-0.20	-0.43	-1.09
Roland Ratzloff #1	3B	0.709234+-7	0.01	-0.13	-1.27
Kulhmeier #1	3B	0.709218+-8	0.30	0.49	-1.22
Morrison #1	3B	0.710085+-9	0.22	0.37	-0.14
Van Meter # 1	3B	0.709015+-8	0.44	0.88	-0.38
Orland Unrue #2	3B	0.709454+-8	0.79	1.43	-0.09
Regier # 1 (A)	3C	0.708604+-9	-0.31	-0.53	-0.20
Kriley G2	3C	0.708785+-8	0.49	0.97	-0.78
Boles F - 1	3C	0.71549+-8	-0.16	-0.51	0.47
Franze E-1	3C	0.70897+-2	0.10	0.22	0.17
James O'Dea A-1	3C	0.71629+-9	0.31	0.34	0.00
Charles 1-12	3C	0.708721+-9	0.30	0.52	0.04
Hanke A-1	3C	0.709235+-8	0.52	0.94	0.07
USA No. AD-2	3C	0.711462+-8	-0.01	-0.29	-0.02
Mowrey W.H. #1	3C	0.710022+-8	1.29	2.80	0.98
Rathjen #1	3C	0.710688+-7	-0.11	0.07	-0.35
Straily	3C	0.70898+-10	0.06	0.12	0.09

Table B.8 Saturation indices for the WIP

Well name	Group	Barite log IAP/KT	Kspar log IAP/KT	Kmica log IAP/KT	Kspar log IAP/KT	Illite log IAP/KT
Groening # 1	2B	1.35	-2.40	5.66	-2.39	-1.07
Fernback J #1	2B	NA	NA	NA	-1.72	-2.03
Cooley #4	2B	0.40	0.05	8.31	0.05	1.69
Cooley #1	2B	0.31	-0.42	8.03	-0.42	1.43
Shear "A"	2B	0.40	0.28	8.73	0.28	2.04
Von Lintel #2	2B	0.55	0.19	9.61	0.19	2.51
Miller #4	2B	0.50	0.89	10.63	NA	NA
UPRC 1-35	2B	0.85	1.93	10.78	1.93	3.97
Kriley E2	2C	0.74	1.83	11.05	1.55	4.00
George West	2C	1.81	1.50	11.34	1.49	4.37
Schmalzried	2C	0.74	1.96	11.62	1.96	4.69
Wiltrout #1	2C	0.63	0.60	9.27	0.60	2.48
Warren #1	2C	0.70	0.30	8.78	0.30	2.11
Holley #201	2C	0.66	2.38	11.68	2.38	4.83
Ray "A" #4	2C	0.71	0.98	10.32	0.98	3.18
Ray "A" #4*	2C	NA	NA	NA	NA	NA
Hart # 1 LSE	3B	2.09	-0.05	9.84	-0.05	2.72
Roland Ratzloff #1	3B	1.91	2.25	12.01	2.25	5.27
Kulhmeier #1	3B	1.59	0.82	10.05	0.82	3.28
Morrison #1	3B	1.47	2.55	11.73	2.55	5.30
Van Meter # 1	3B	3.04	2.30	12.48	2.29	5.67
Orland Unrue #2	3B	1.43	1.69	11.50	1.69	4.62
Regier # 1 (A)	3C	3.14	NA	NA	NA	NA
Kriley G2	3C	2.02	3.67	14.53	3.68	7.57
Boles F - 1	3C	2.73	4.83	15.82	4.79	8.74
Franze E-1	3C	2.10	NA	NA	NA	NA
James O'Dea A-1	3C	2.18	3.14	15.67	3.14	7.75
Charles 1-12	3C	NA	NA	NA	NA	NA
Hanke A-1	3C	2.92	NA	NA	NA	NA
USA No. AD-2	3C	3.27	4.41	16.27	4.42	9.23
Mowrey W.H. #1	3C	1.94	4.58	15.71	4.58	8.73
Rathjen #1	3C	2.12	4.38	15.83	4.38	8.66
Straily	3C	1.98	2.40	13.03	2.40	5.66

In samples were NA is reported the saturation indices were below -3.

Table B.9 Geochemical rations and carpenter function for the WIP

Well name	Group	Cl/Br mg/l	Na/Br mg/l	C.F. meq/l	K/Rb
Groening # 1	2B	271	145	97	901
Fernback J #1	2B	211	155	-73	884
Cooley #4	2B	459	293	116	NA
Cooley #1	2B	1,184	859	-12	NA
Shear "A"	2B	650	408	60	NA
Von Lintel #2	2B	543	349	131	NA
Miller #4	2B	558	306	79	NA
UPRC 1-35	2B	2,352	1,891	-108	NA
Kriley E2	2C	349	172	92	700
George West	2C	383	200	159	829
Schmalzried	2C	290	140	85	355
Wiltrout #1	2C	945	628	93	NA
Warren #1	2C	1,158	787	117	NA
Holley #201	2C	3,420	2,522	34	NA
Ray "A" #4	2C	1,257	867	92	NA
Ray "A" #4*	2C	NA	NA	95	NA
Hart # 1 LSE	3B	324	163	227	962
Roland Ratzloff #1	3B	363	170	164	895
Kulhmeier #1	3B	339	172	204	867
Morrison #1	3B	347	156	251	794
Van Meter # 1	3B	348	161	245	911
Orland Unrue #2	3B	277	142	248	835
Regier # 1 (A)	3C	260	125	765	608
Kriley G2	3C	372	161	413	983
Boles F - 1	3C	283	134	547	451
Franze E-1	3C	289	142	598	874
James O'Dea A-1	3C	292	132	532	541
Charles 1-12	3C	273	126	713	906
Hanke A-1	3C	273	127	718	752
USA No. AD-2	3C	275	121	926	390
Mowrey W.H. #1	3C	285	146	423	1197
Rathjen #1	3C	333	182	235	1216
Straily	3C	2,272	1,446	310	NA

Table B.10 Location, formation and age for the GP and blank and replicate data

Well name	Group	County/State	Formation	Age
Ben #1	GP1	Washington Co., CO	J Sand	GP/CRE
Well 5 Ranger Fed	GP1	Lane Co., KS	Dakota	GP/CRE
Well 3 Poky Fed	GP1	Scott Co., KS	Dakota	GP/CRE
Dakota # 2 Sunflower	GP1	Finney Co., KS	Dakota	GP/CRE
Charvie Well	GP1	Banner Co., NE	Transitional Pierre	GP/CRE
Shanaman #2	GP1	Scotts Bluff, NE	Massive J	GP/CRE
Artesian Hall	GP1	Morril Co., NE	Chadron	GP/TER(OLIG)
Leoti #13	GP1	Wichita, KS	Dakota	GP/CRE
Dakota #2-Hays	GP1	Ellis Co., KS	Dakota	GP/CRE
MNJSU #6	GP1	Logan Co., CO	J Sand	GP/CRE
Hart #1	GP2	Morril Co., NE	J Sand	GP/CRE
Graf #1	GP2	Cheyenne Co., NE	J Sand	GP/CRE
Day #1	GP2	Cheyenne Co., NE	D Sand	GP/CRE
UPRR 1-1	GP2	Cheyenne Co., CO	Dakota	GP/CRE
Lowe #3	GP2	Cheyenne Co., CO	Dakota	GP/CRE
Perot 7-1	GP2	Cheyenne Wells, CO	Dakota	GP/CRE
Schwake "A" #2	GP2	Logan Co., CO	J Sand	GP/CRE
Blank @ Regier	NA	Harvey, KS	NA	NA
Blank @ USA	NA	Morton, Ks	NA	NA
Blank @ OK	NA	Texas, Ok	NA	NA
Blank @ lab	NA	NA	NA	NA
Blank @ Ben #1	NA	Washington Co., CO	NA	NA
Blank @ Graf #1	NA	Cheyenne Co., NE	NA	NA
Blank @ Straily	NA	Ellis, Ks	NA	NA
Dakota #2 Hays (replicate)	GP1	Ellis Co, KS	Dakota	GP/CRE
Rathjen #1 (replicate)	WIP (3C)	Texas Co., OK	Krider	WIP/PENN

Table B.11 Well depth, pH, temperature, Eh, and conductivity for the GP

Well name	Group	Well depth	pH	T C	Eh	Conductivity ms/cm
Ben #1	GP1	NA	7.95	28.3000	-53	29
Well 5 Ranger Fed	GP1	283	7.57	21.4	-63	2.03
Well 3 Poky Fed	GP1	NA	7.36	40.1	-334	74.46
Dakota # 2 Sunflower	GP1	226	7.24	21.8	31	15.3
Charvie Well	GP1	NA	8.5	21.4	-63	2.03
Shanaman #2	GP1	NA	7.96	40.1	-334	74.46
Artesian Hall	GP1	15	7.94	21.8	31	15.3
Leoti #13	GP1	NA	8.57	24	-111	1.71
Dakota #2-Hays	GP1	792	8	24.8	-51	3.9
MNJSU #6	GP1	NA	8.24	38.5	-249	40
Hart #1	GP2	1,219	6.75	31.1	-118	159.9
Graf #1	GP2	NA	6.97	39	-189	113.2
Day #1	GP2	NA	8.06	36.1	-346	127.3
UPRR 1-1	GP2	NA	6.83	30.3	-150	37
Lowe #3	GP2	NA	6.69	36.5	-267	44.5
Perot 7-1	GP2	320	7.51	36.1	-266	19
Schwake "A" #2	GP2	NA	7.71	35.80	-323	15.85
Blank @ Regier	NA	NA	NA	NA	NA	NA
Blank @ USA	NA	NA	NA	NA	NA	NA
Blank @ OK	NA	NA	NA	NA	NA	NA
Blank @ lab	NA	NA	NA	NA	NA	NA
Blank @ Ben #1	NA	NA	NA	NA	NA	NA
Blank @ Graf #1	NA	NA	NA	NA	NA	NA
Blank @ Straily	NA	NA	NA	NA	NA	NA
Dakota #2 Hays (replicate)	GP1					
Rathjen #1 (replicate)	3C					

Table B.12 TDS and geochemical data for the GP, blanks, and replicates

Well name	Group	TDS mg/l	Cl mg/l	SO_4 mg/l	Br mg/l	NO_3 mg/l	HCO_3 mg/l
Ben #1	GP1	2394	330	84	2	<0.005	1,220
Well 5 Ranger Fed	GP1	1238	227	10	2	<0.005	854
Well 3 Poky Fed	GP1	560	938	583	6	<0.005	2,330
Dakota # 2 Sunflower	GP1	376	153	214	2	<0.005	366
Charvie Well	GP1	1593.444	227	10	2	<0.005	854
Shanaman #2	GP1	5667.132	938	583	6	<0.005	2,330
Artesian Hall	GP1	1036.025	153	214	2	<0.005	366
Leoti #13	GP1	1,240	64	413	1	3.74	365
Dakota #2-Hays	GP1	2,087	575	283	0	0.33	360
MNJSU #6	GP1	2,982	560	85	5	<0.005	1,342
Hart #1	GP2	129,843	73,631	2,561	27	<0.005	317
Graf #1	GP2	82,329	45,290	3,300	8	<0.005	625
Day #1	GP2	8,933	2,852	407	14	<0.005	2,513
UPRR 1-1	GP2	23,912	12,269	1,844	8	<0.005	159
Lowe #3	GP2	28,895	14,619	1,882	7	<0.005	195
Perot 7-1	GP2	14,282	7,034	2,370	35	<0.005	253
Schwake "A" #2	GP2	10,934	3,942	514	17	<0.005	2,440
Blank @ Regier	NA	--	<0.005	<0.005	<0.005	<0.005	<0.005
Blank @ USA	NA	0	<0.005	<0.005	<0.005	<0.005	<0.005
Blank @ OK	NA	0	<0.005	<0.005	<0.005	<0.005	<0.005
Blank @ lab	NA		<0.005	<0.005	<0.005	<0.005	<0.02
Blank @ Ben #1	NA		<0.005	<0.005	<0.005	<0.005	<0.02
Blank @ Graf #1	NA		<0.005	<0.005	<0.005	<0.005	<0.02
Blank @ Straily	NA		<0.005	<0.005	<0.005	<0.005	<0.02
Dakota #2 Hays (replicate)	GP1		943	297	0.4	0.55	
Rathjen #1 (replicate)	WIP (3C)		149,284	1730	56	39.25	

Table B.13 Geochemical data for the GP, blanks, and replicates

Well name	Group	Li mg/l	B 11 mg/l	Na mg/l	Mg mg/l	Al mg/l	Si mg/l
Ben #1	GP1	0.36		737	0	0.03	17.07
Well 5 Ranger Fed	GP1	0.21		485	1	0.03	6.40
Well 3 Poky Fed	GP1	0.74		1,782	1	0.03	16.43
Dakota # 2 Sunflower	GP1	0.13		277	3	0.03	5.74
Charvie Well	GP1	0.21		485	1	0.03	6.40
Shanaman #2	GP1	0.74		1,782	1	0.03	16.43
Artesian Hall	GP1	0.13		277	3	0.03	5.74
Leoti #13	GP1	0.10	0.91	380	3	0.01	4.02
Dakota #2-Hays	GP1	0.44		833	8	0.03	4.33
MNJSU #6	GP1	0.48		969	0	0.03	20.15
Hart #1	GP2	26.00		50,349	395	0.06	11.01
Graf #1	GP2	17.50		31,832	235	0.09	9.01
Day #1	GP2	2.03		3,098	1	0.03	19.74
UPRR 1-1	GP2	12.70		8,282	143	0.06	15.46
Lowe #3	GP2	18.53		10,407	183	0.06	15.62
Perot 7-1	GP2	6.95	5.08	3,695	126	0.01	14.80
Schwake "A" #2	GP2	3.11		3,932	2	0.03	21.98
Blank @ Regier		0.00	0.00	0	0	0	0.02
Blank @ USA		0.08	0.00	0	0	0	0.02
Blank @ OK		0.00	0.00	0	0	0	0.02
Blank @ lab			<0.1	<0.005	0	0	
Blank @ Ben #1			<0.1	<0.005	0	0	
Blank @ Graf #1			<0.1	<0.005	0	0	
Blank @ Straily			<0.1	<0.005	0	0	
Dakota #2 Hays (replicate)	GP1	0.02	1.36	851	9	0.004	4.93
Rathjen #1 (replicate)	WIP (3C)			87,660	1369		

Table B.14 Geochemical data for the GP, blanks, and replicates

Well name	Group	P mg/l	K mg/l	Ca mg/l	Fe mg/l	Mn mg/l	Rb mg/l
Ben #1	GP1		5	0	0.01	0.01	
Well 5 Ranger Fed	GP1		8	2	0.01	0.01	
Well 3 Poky Fed	GP1		10	5	0.01	0.01	
Dakota # 2 Sunflower	GP1		7	10	0.01	0.01	
Charvie Well	GP1		8	2	0.01	0.01	
Shanaman #2	GP1		10	5	0.01	0.01	
Artesian Hall	GP1		7	10	0.01	0.01	
Leoti #13	GP1	0.01	5	6	0.25	0.02	0.01
Dakota #2-Hays	GP1		15	7	0.01	0.01	
MNJSU #6	GP1		5	0	0.01	0.01	
Hart #1	GP2		605	1,833	31.12	1.26	
Graf #1	GP2		270	713	0.50	0.15	
Day #1	GP2		35	3	0.01	0.15	
UPRR 1-1	GP2		260	900	0.10	0.10	
Lowe #3	GP2		370	1,167	0.10	0.10	
Perot 7-1	GP2	0.00	87	670	0.08	0.07	0.52
Schwake "A" #2	GP2		65	13	0.01	0.01	
Blank @ Regier		0.08	0	0.1	0.00	0.00	0.00
Blank @ USA		0.08	0	0.1	0.00	0.00	0.00
Blank @ OK		0.09	0	0.09	0.00	0.00	0.00
Blank @ lab		<0.1	<0.01	<0.005	<0.005		<0.005
Blank @ Ben #1		<0.1	<0.01	<0.005	<0.005		<0.005
Blank @ Graf #1		<0.1	<0.01	<0.005	<0.005		<0.005
Blank @ Straily		<0.1	<0.01	<0.005	<0.005		<0.005
Dakota #2 Hays (replicate)	GP1	0.06	7.45	8.52			
Rathjen #1 (replicate)	WIP (3C)			3350			

Table B.15 Geochemical and isotopic data for the GP, blanks, and replicates

Well name	Group	Sr mg/l	Ba mg/	Pb mg/	Charge Balance	$\delta^{18}O$	δD
Ben #1	GP1	0.23	0.10	0.05	-2.71	-12	-94
Well 5 Ranger Fed	GP1	0.23	0.04	0.05	-2.55	-13	-96
Well 3 Poky Fed	GP1	0.94	0.05	0.05	-3.61	-10	-81
Dakota # 2 Sunflower	GP1	0.36	0.01	0.05	-4.56	-13	-101
Charvie Well	GP1	0.23	0.04	0.05	-2.60	-13	-96
Shanaman #2	GP1	0.94	0.05	0.05	-1.17	-10	-81
Artesian Hall	GP1	0.36	0.01	0.05	5.84	-13	-101
Leoti #13	GP1	0.15	0.02	0.00	-3	-12	-84
Dakota #2-Hays	GP1	0.20	0.01	0.05	-8.5	-12	-92
MNJSU #6	GP1	0.12	0.26	0.05	-4	-10	-85
Hart #1	GP2	78	0.17	2.05	-4	-7	-68
Graf #1	GP2	34	0.15	1.50	-3	-10	-89
Day #1	GP2	0.50	0.09	0.05	-2	-5	-55
UPRR 1-1	GP2	26	0.10	1.00	-5	-12	-90
Lowe #3	GP2	36	0.10	1.00	-9	-10	-87
Perot 7-1	GP2	20	0.83	0.00	9	-11	-83
Schwake "A" #2	GP2	1	0.05	0.05	-4	-4	-57
Blank @ Regier		0	0.00				
Blank @ USA		0	0.00				
Blank @ OK		0	0.00				
Blank @ lab		<0.005	<0.05	<0.005			
Blank @ Ben #1		<0.005	<0.05	<0.005			
Blank @ Graf #1		<0.005	<0.05	<0.005			
Blank @ Straily		<0.005	<0.05	<0.005			
Dakota #2 Hays (replicate)	GP1	0.21			-8		
Rathjen #1 (replicate)	WIP (3C)	91			-5		

Table B.16 Strontium isotopic data and saturation indices for the GP, blanks, and replicates

Well name	Group	$^{87}Sr/^{86}Sr$	Calcite log IAP/KT	Dolomite log IAP/KT	Gypsum log IAP/KT
Ben #1	GP1	0.70774+-7	-1.20	-3.71	-4.36
Well 5 Ranger Fed	GP1	0.70887+-8	0.11	0.14	-1.88
Well 3 Poky Fed	GP1	0.70807+-9	-0.39	-0.71	-2.03
Dakota # 2 Sunflower	GP1	0.70938+-6	-0.73	-0.94	-1.92
Charvie Well	GP1	0.70887+-9	0.04	0.12	-4.30
Shanaman #2	GP1	0.70807+-7	0.25	0.14	-2.62
Artesian Hall	GP1	0.70938+-7	-0.14	-0.29	-2.21
Leoti #13	GP1	0.708111+-8	0.16	0.31	-2.28
Dakota #2-Hays	GP1	0.70850+-7	-0.29	-0.16	-2.42
MNJSU #6	GP1	0.70847+-7	-2.25	-4.28	-5.88
Hart #1	GP2	0.70814+-9	0.53	0.94	-0.15
Graf #1	GP2	0.70817+-9	0.65	1.38	-0.45
Day #1	GP2	0.70870+-9	0.15	0.10	-3.03
UPRR 1-1	GP2	0.73045+-8	-0.03	-0.42	-0.31
Lowe #3	GP2	0.73189+-9	0.09	-0.15	-0.27
Perot 7-1	GP2	0.72989+-8	0.83	1.37	-0.19
Schwake "A" #2	GP2	0.70895+-8	0.16	0.05	-2.34
Blank @ Regier					
Blank @ USA					
Blank @ OK					
Blank @ lab					
Blank @ Ben #1					
Blank @ Graf #1					
Blank @ Straily					

Table B.17 Saturation indices for the GP

Well name	Group	Barite log IAP/KT	Kspar log IAP/KT	Kmica log IAP/KT	Kspar log IAP/KT	Illite log IAP/KT
Ben #1	GP1	0.02	-0.32	6.15	-0.32	-0.14
Well 5 Ranger Fed	GP1	-0.28	-0.68	7.08	-0.68	0.87
Well 3 Poky Fed	GP1	-0.58	-1.21	6.93	-1.21	0.63
Dakota # 2 Sunflower	GP1	-0.20	-1.42	7.00	-1.42	0.71
Charvie Well	GP1	-1.06	-0.90	5.12	-0.90	-0.67
Shanaman #2	GP1	0.01	-0.95	4.46	-0.95	-1.11
Artesian Hall	GP1	-0.38	-1.07	6.04	-1.07	-0.08
Leoti #13	GP1	0.02	-2.49	2.07	-2.49	-3.13
Dakota #2-Hays	GP1	-0.78	-1.37	5.31	-1.37	-0.74
MNJSU #6	GP1	0.21	-0.88	4.14	-0.88	-1.61
Hart #1	GP2	1.24	2.62	12.33	2.62	5.32
Graf #1	GP2	0.83	0.96	9.64	0.96	2.92
Day #1	GP2	0.07	0.08	5.60	0.08	-0.15
UPRR 1-1	GP2	0.49	1.43	10.41	1.43	3.55
Lowe #3	GP2	0.36	1.19	9.92	1.19	3.10
Perot 7-1	GP2	0.49	-0.27	5.51	-0.27	-0.04
Schwake "A" #2	GP2	-0.11	0.54	6.76	0.54	0.80
Blank @ Regier						
Blank @ USA						
Blank @ OK						
Blank @ lab						
Blank @ Ben #1						
Blank @ Graf #1						
Blank @ Straily						

Table B.18 Geochemical ratios and carpenter function for the GP

Well name	Group	Cl/Br mg/l	Na/Br mg/l	C.F. meq/l	K/Rb
Ben #1	GP1	220	491	-22	
Well 5 Ranger Fed	GP1	1,827	2,429	-7	
Well 3 Poky Fed	GP1	900	3,967	-4	
Dakota # 2 Sunflower	GP1	193	1,445	-2	
Charvie Well	GP1	127	271	-14	
Shanaman #2	GP1	147	280	-50	
Artesian Hall	GP1	84	152	-10	
Leoti #13	GP1	63	376	-14	828
Dakota #2-Hays	GP1	2,614	3,786	-11	
MNJSU #6	GP1	105	182	-24	
Hart #1	GP2	2,727	1,865	67	
Graf #1	GP2	5,661	3,979	-23	
Day #1	GP2	210	228	-49	
UPRR 1-1	GP2	1,461	986	16	
Lowe #3	GP2	2,215	1,577	32	
Perot 7-1	GP2	201	106	-9	167
Schwake "A" #2	GP2	232	231	-50	
Blank @ Regier					
Blank @ USA					
Blank @ OK					
Blank @ lab					
Blank @ Ben #1					
Blank @ Graf #1					
Blank @ Straily					

Table B.19 Oxygen, hydrogen, strontium isotope replicates for the WIP

Well Name	$\delta^{18}O$	$\delta^{18}O$ replicate	δD	δD replicate	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr$ replicate
Boles F - 1	-2.73		-34.1	-34.1	0.715489+-8	
Charles 1-12	0.78		-26.1		0.708721+-9	
Cooley #1	-10.04		-77.14		.718209+-7	
Cooley #4	-8.3		-76.16		0.710261 +-8	
Fernback J #1	-9.13		-62		0.709085+-8	0.709087+-8
Franze E-1	0.76		-24.9		0.708981+-9	
George West	-7.97	-7.99	-69.1		0.713031+-7	
Groening # 1	-10.92		-89.2	-88.7	0.711141+-8	
Hanke A-1	0.44		-21.1		0.709235+-8	
Hart # 1 LSE	-4.13		-44.9		0.709207+-8	0.709209+-8
Holley #201	-7.22		-66.81		0.710953+-6	
James O'Dea A-1	-3.42		-36		0.716295+-9	
Kriley E2	-6.23		-66.7		0.713288+-8	
Kriley G2	-3.08		-45.4	-45.2	0.708785+-8	
Kulhmeier #1	-3.6		-42.3		0.709218+-8	
Miller #4	-8.45		-73.5			
Morrison #1	-6.99		-64.3	-63.7	0.710085+-9	
Mowrey W.H. #1	-0.69		-27.4		0.710022+-8	
Orland Unrue #2	-5.31		-55.6		0.709454+-8	
Rathjen #1	-1.93	-2.63	-29.3		0.710688+-7	
Ray "A" #4	-4.35		-56.49		0.715709+-12	
Regier # 1 (A)	1.40	1.32	-16.7		0.708604+-9	
Roland Ratzloff #1	-3.48		-41.6		0.709234+-7	
Schmalzried	-8.31		-65.4		0.718604+-9	
Shear "A"	-9.93		-79.2		0.724762+-7	
Straily	-0.29	0.06	-36.9	-31.37	0.708978+-10	
UPRC 1-35	-7.19		-83		0.708977+-9	
USA No. AD-2	0.71		-18.3	-20.1	0.711462+-8	
Van Meter # 1	-4.10	-4.10	-45.9		0.709015+-8	
Von Lintel #2	-8.65	-8.79	-77.3		0.720940+-9	
Warren #1	-4.51		-54		0.723720+-7	
Wiltrout #1	-4.46		-59.45	-61.06	0.715845+-7	

George West, Von Meter #1, and Von Meter #2 oxygen replicates were equilibrated for 24 hours. Rathjen #1, Regier #1A, and Straily oxygen replicates were equilibrated for 36 hours due to their high salinity. See analytical methods section in Appendix A for details.

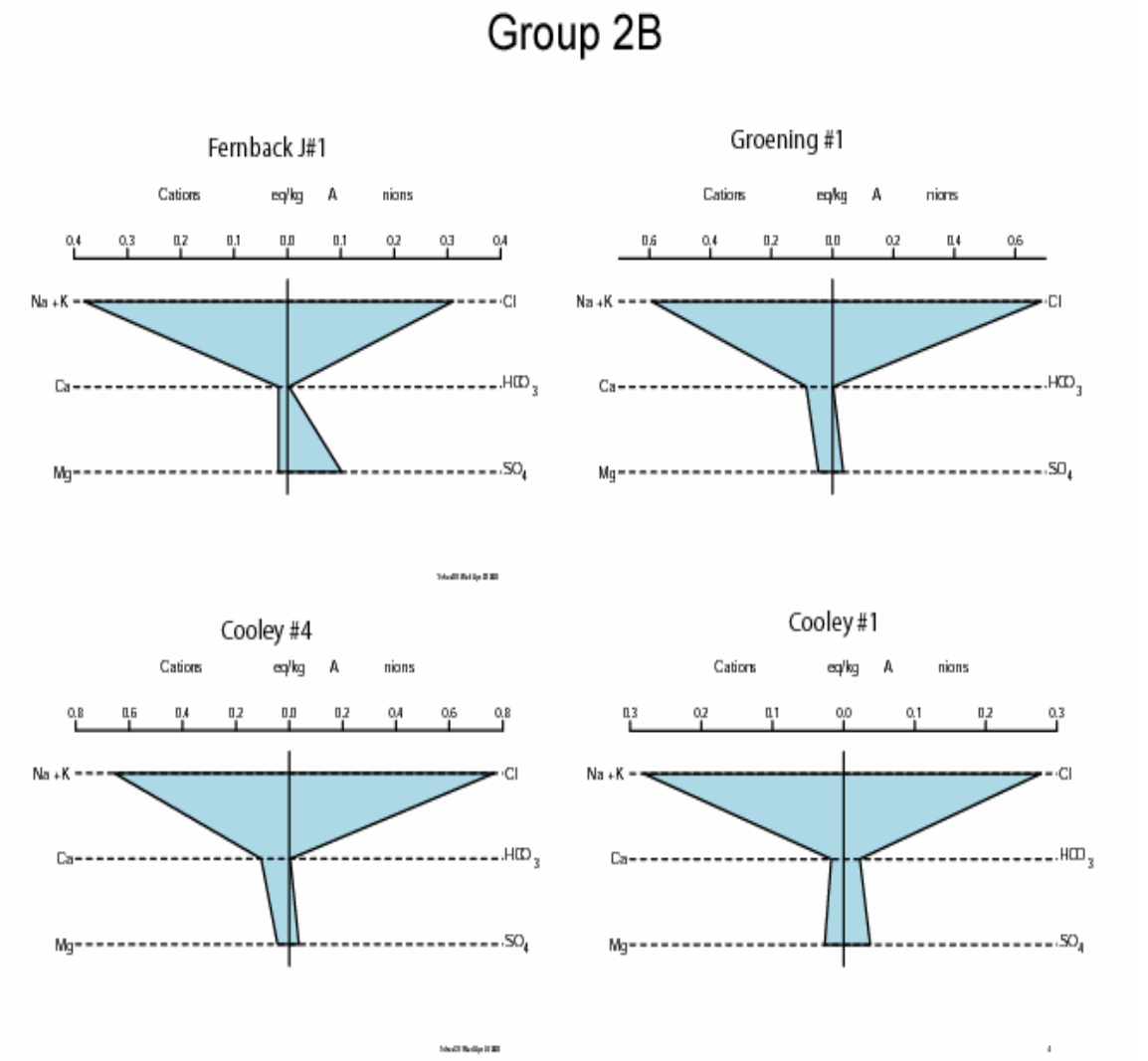
Table B.20 Oxygen, hydrogen, strontium isotope replicates for the GP

Well Name	$\delta^{18}O$	$\delta^{18}O$ replicate	$\delta^{18}O$ replicate	δD	δD replicate	$^{87}Sr/^{86}Sr$
Artesian Hall	-13.37			-100.7		0.709380+-7
Ben #1	-12.01			-94.07		0.707747+-7
Charvie Well	-12.75			-95.6		0.708765+-9
Dakota # 2 Sunflower	-11.39			-88.4		0.709056+-6
Dakota #2-Hays	-11.83			-91.5		0.708504+-7
Day #1	-4.63			-55.04		0.708701+-9
Graf #1	-10.3			-89.21		0.708175+-9
Hart #1	-6.65			-67.5		0.708139+-9
Leoti #13	-11.75			-83.7		0.708111+-8
Lowe #3	-11.40	-11.25		-87.37	-85.77	0.731891+-9
MNJSU #6	-10.40	-10.67		-84.75		0.708467+-8
Perot 7-1	-11.06	-11.08		-83.3		0.729884+-9
Schwake "A" #2	-4.14			-56.97		0.708946+-8
Shanaman #2	-10.31	-10.24	-10.26	-81.1	-83.61	0.708074+-7
UPRR 1-1	-11.52			-89.8		0.730445+-8
Well 3 Poky Fed	-12.07			-94.1		0.708804+-9
Well 5 Ranger Fed	-11.68			-90.39		0.708758+-8
City Well #33-Hays	-7.9				-65	0.708614+-8

All oxygen replicates were equilibrated for 24 hours.

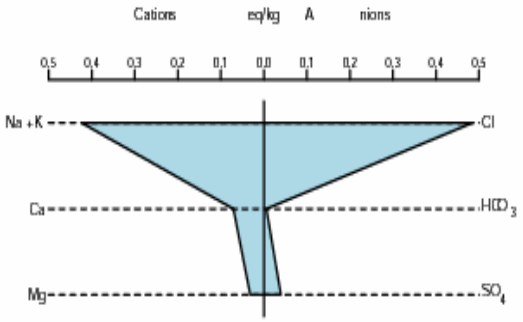
Appendix C

Stiff Diagrams

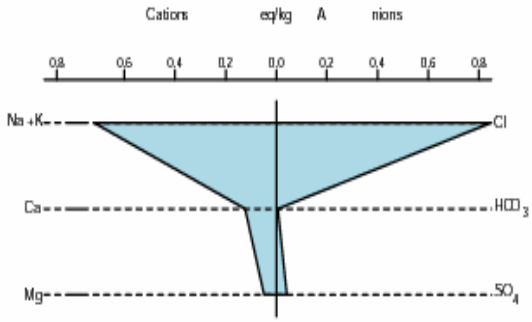


Group 2B

Shear "A"



Von Lintel #2



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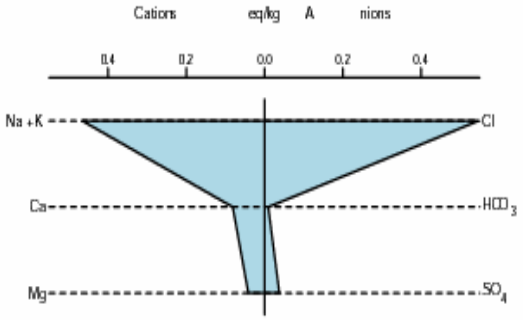
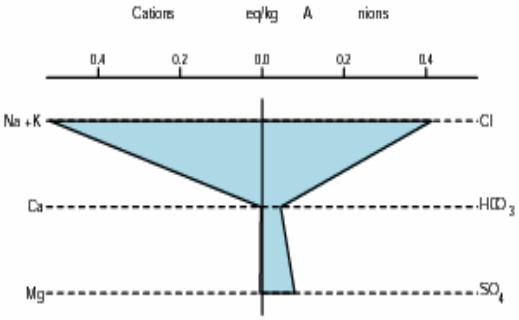


UPRC 1-35



Group 2C

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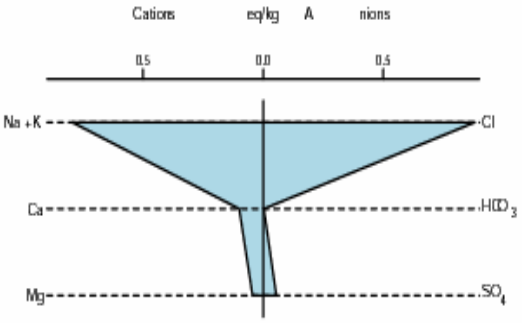

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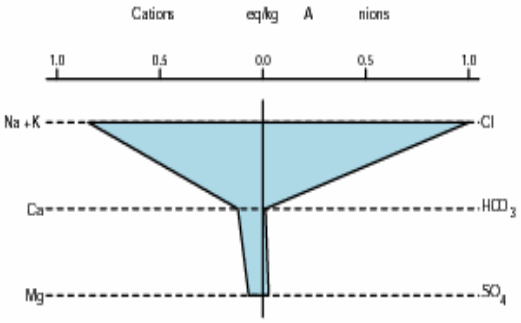
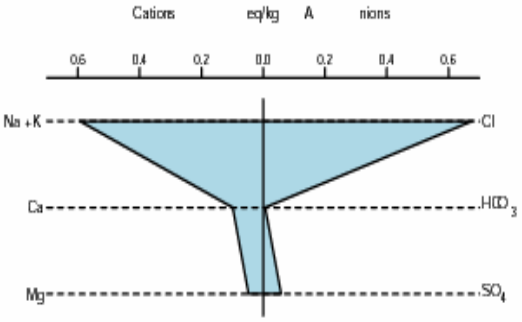


Schmalzried



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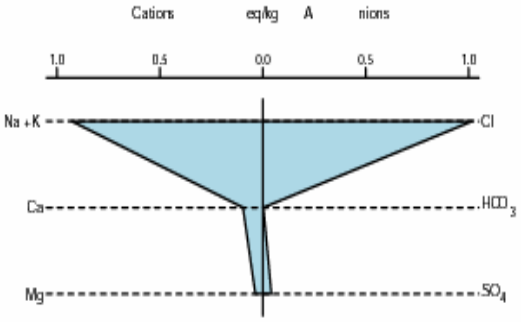

Group 2C

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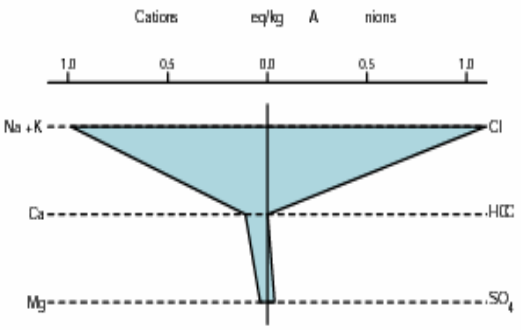

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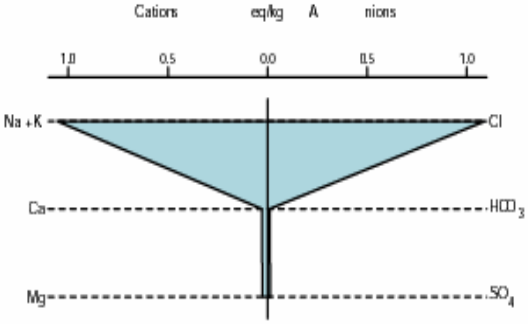

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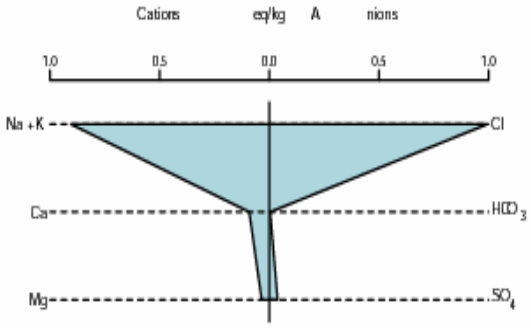
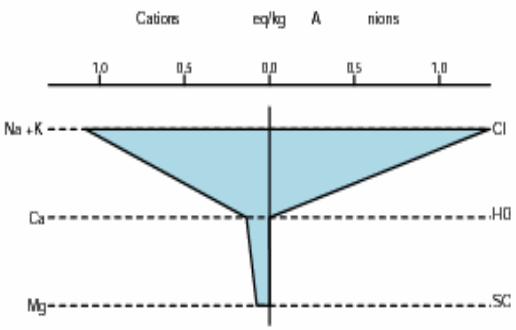


Group 3B

Hart #1 LSE



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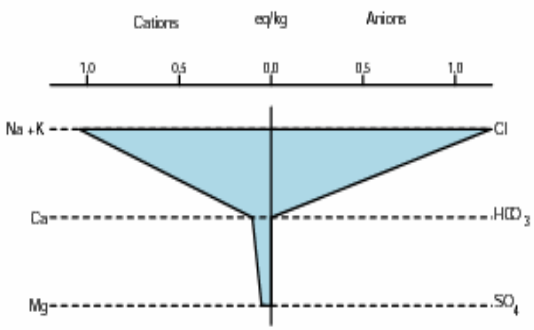

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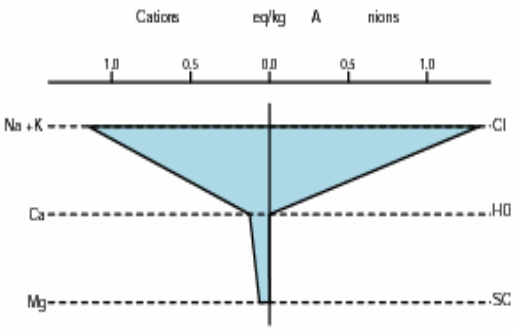

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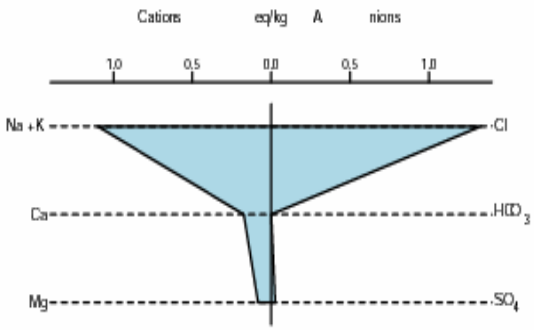

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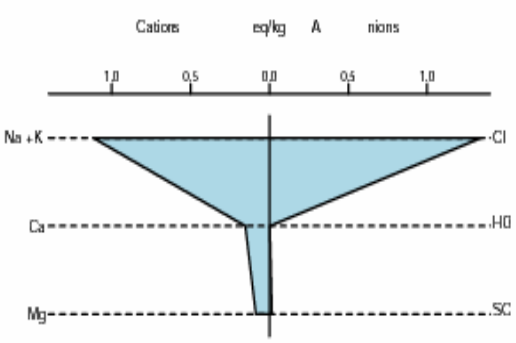

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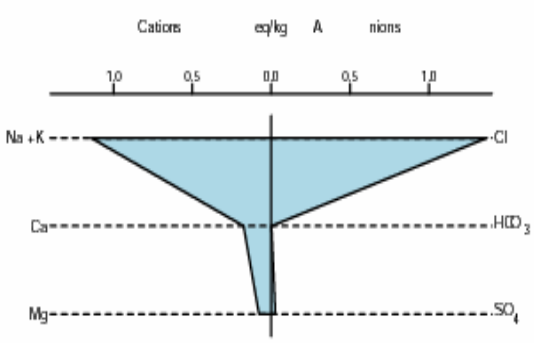
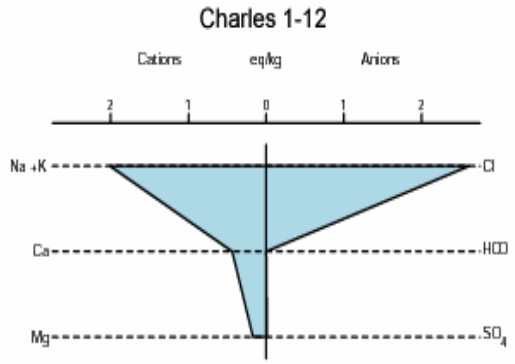


Group 3C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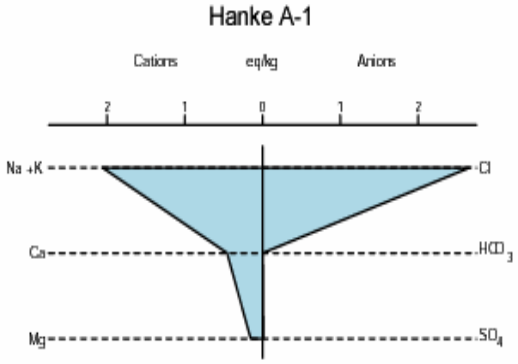
Cations
eq/kg
Anions
2 1 0 1 2
Na +K
Ca
Mg
Cl
HCO
SO4


Hanke A-1
Cations
eq/kg
Anions
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Mg
Cl
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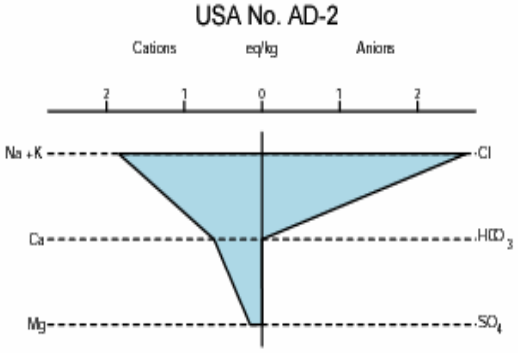
USA No. AD-2
Cations
eq/kg
Anions
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Ca
Mg
Cl
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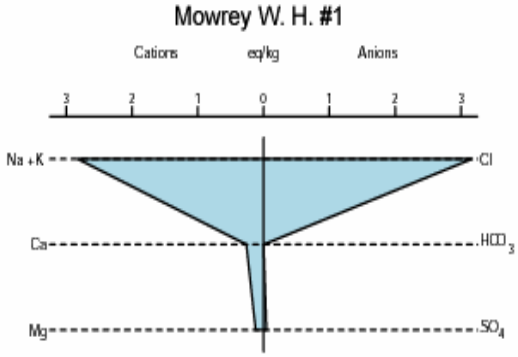
SO4


Mowrey W. H. #1
Cations
eq/kg
Anions
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Ca
Mg
Cl
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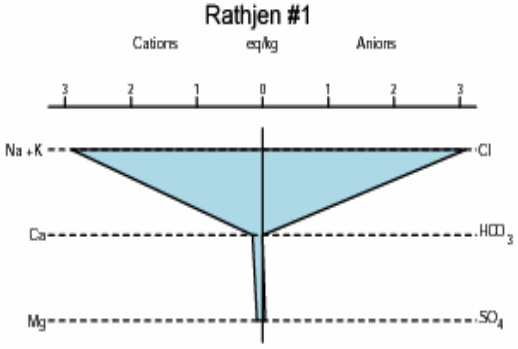
Rathjen #1
Cations
eq/kg
Anions
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Na +K
Ca
Mg
Cl
HCO3
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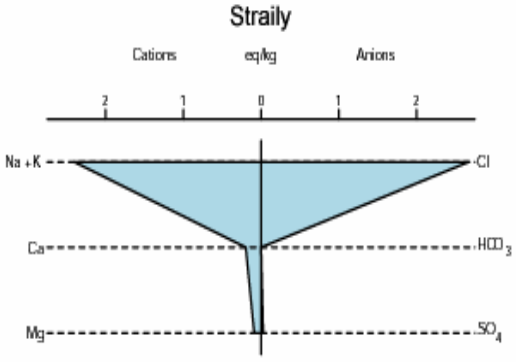
Straily
Cations
eq/kg
Anions
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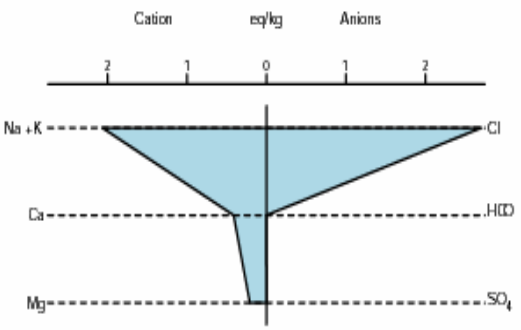
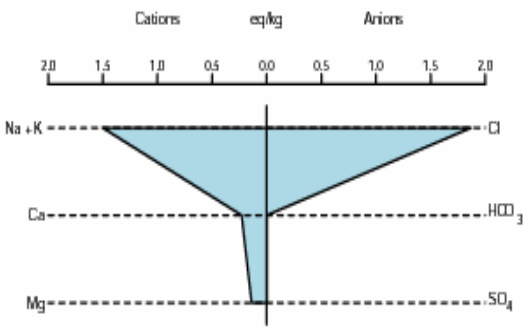
Na +K
Ca
Mg
Cl
HCO3
SO4

Group 3C

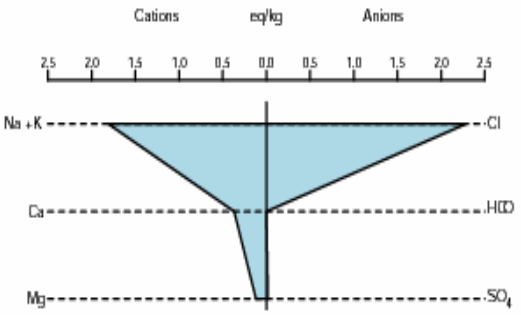
Regier #1 A



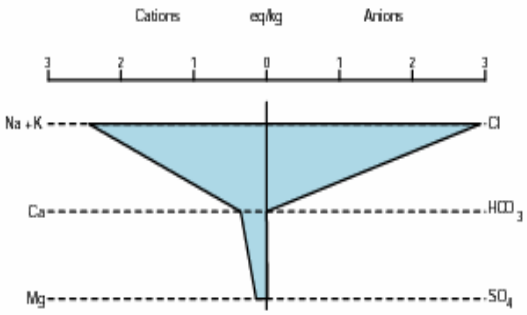
Kriley G2



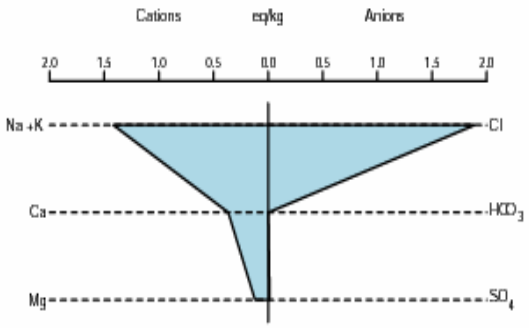
Boles F-1



Franze E-1

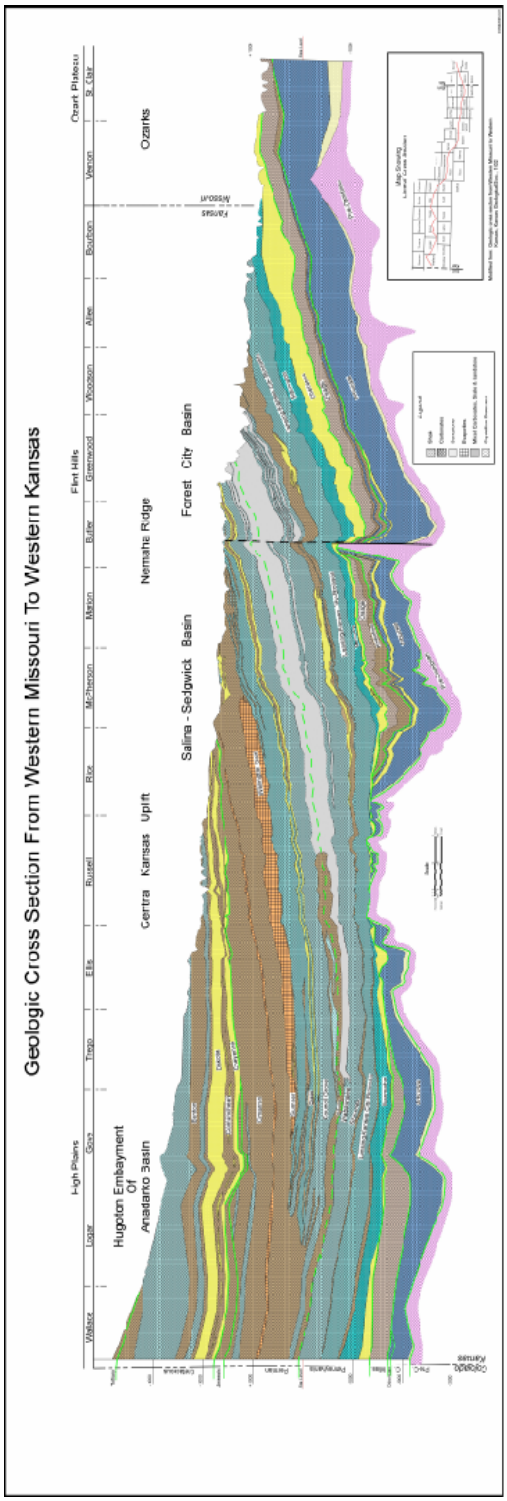


James O'Dea A-1

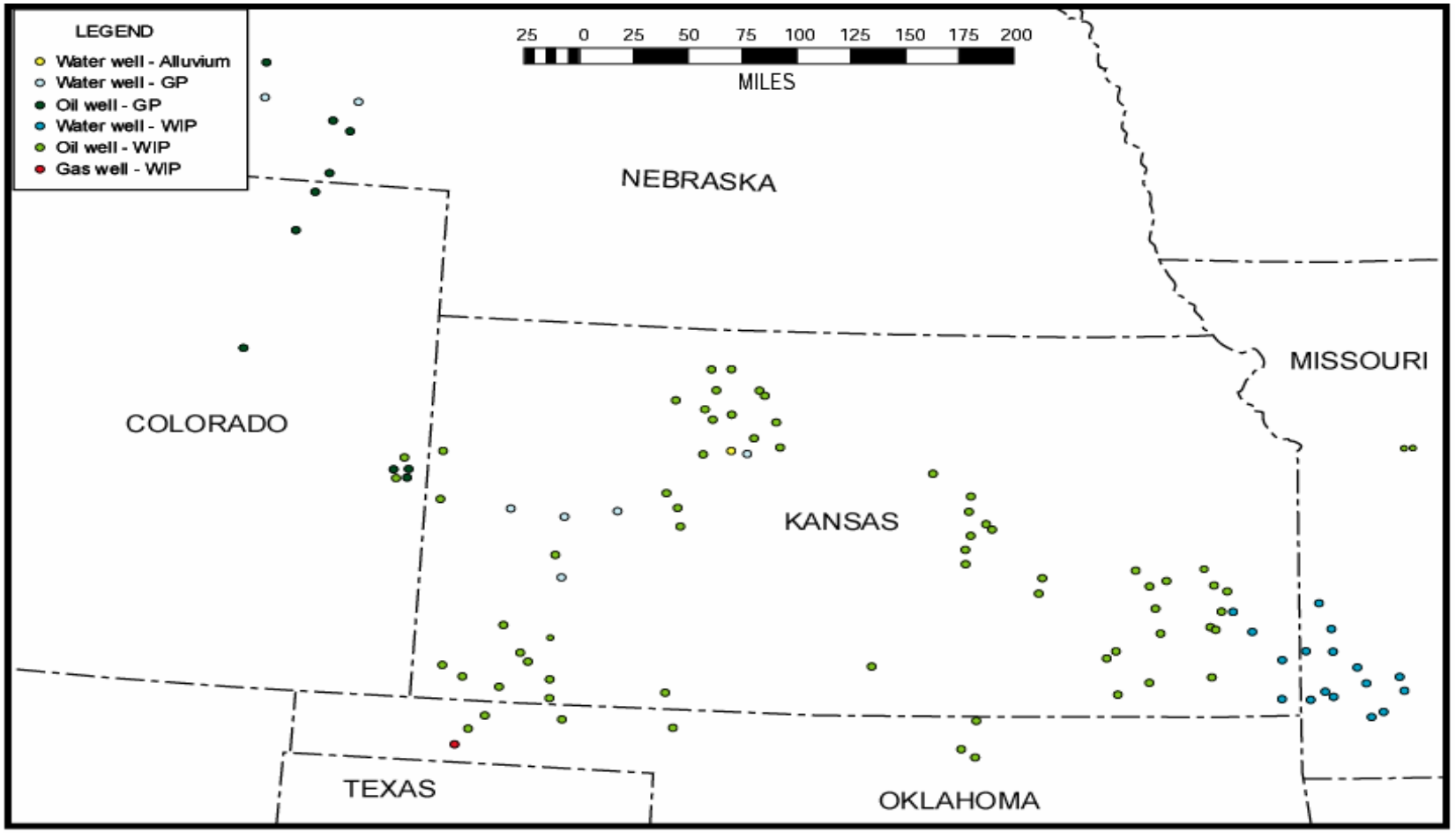


Appendix D

Mid-continent cross section



Appendix D
Detailed cross section of the mid-continent, from western Kansas to eastern Missouri. Zoom in for more detail. Modified from Kansas Geological Survey (1932)



Map showing the location of the gas, oil and water wells in the study area. This map includes data from Musgrove and Banner (1993), Nicastro (1983), and Chadhuri et al. (1987, 1992).

Bibliography

Bachu, S., 1995, Synthesis and Model of Formation-Water Flow, Alberta Basin, Canada, AAPG Bulletin, Vol. 79, No. 8, pp. 1159-1178.

Bachu, S, Brulotte, M. Grobe, M, and Stewart, S., 2000, The sustainability of the Alberta subsurface for carbon dioxide sequestration in geological media, Earth Science Report, March 2000, 86 p.

Banner, J. L. and Hanson, G N., 1990, Calculations of simultaneous isotopic and trace element variations during water:rock interaction with applications to carbonate diagenesis, Geochimica et Cosmochimica Acta, Vol. 54, pp. 3123-3137.

Banner, J. L. Hanson, G. N., and Meyers, W. J., 1988, Determination of initial Sr isotopic compositions of dolostones from the Burlington-Keokuk Formation (Mississippian): Constraints from cathodoluminescence, glauconite paragenesis and analytical methods, J. Sediment. Petrol, Vol, 58, pp. 673-687.

Banner, J. L., Musgrove, M., and Capo, R. C., 1994, Tracing Ground-Water Evolution in a Limestone Aquifer Using Sr Isotopes: Effects on Multiple Sources of Dissolved Ions and Mineral-Solution Reactions, Geology, Vol. 22, pp. 687-690.

Banner, J. L., Wasserburg, G. J., Dobson, P. F., Carpenter, A. B., and Moore, C. H., 1989, Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri, Geochimica and Cosmochimica Acta, Vol. 53, pp. 383-398.

Bentley, H. W., Phillips, F. M., Davis, S. N., Habermehl, M. A., Airey, P. L., Calf, G. E., Elmore, D., Gove, H. E., and Torgensen, T., 1986, Chlorine 36 Dating of Very Old Groundwater 1. The Great Artesian Basin, Australia, Water Resources Research, Vol. 22, No. 13, pp. 1991-2001.

Belitz, K., and Bredehoeft, J. D., 1988, Hydrodynamics of the Denver Basin: Explanation to Subnormal Fluid Pressures, AAPG, Vol. 72, No. 11, pp. 1334-1359.

Bethke, C. M, 1994, The Geochemist Workbench, version 2.0, A Users Guide to Rxn, Act2, Tact, React, and Gtplot, Hydrogeology Program, University of Illinois.

Bethke, C. M., and Marshak, S., 1990, Brine migration across North America – The plate tectonics of groundwaters, Annu. Rev. Earth Planet. Sci., Vol. 19, pp. 287-315.

Bredehoeft, J. D., Neuzil, C. E., and Milly, P. C. D., 1983, Regional flow in the Dakota aquifer, a study of the role of confining layers, USGS Water Supply paper No. 2237, 45 p.

Broecker, W. S., and Denton, G. H., 1989, The Role of Ocean-Atmosphere Reorganizations in Global Cycles, Geochimica et Cosmochimica Acta, Vol. 53, pp. 2465-2501.

Bruant, R. G., Celia, M. A., Guswa, A. J., and Peters, C. A., 2002, Safe storage of CO_2 in deep saline aquifers, Environmental Science and Technology, Vol. 36, No. 11, pp. 240-245.

Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982, Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time, Geology Boulder, Vol. 10, Issue 10, pp. 516-519.

Burrus, R. C., and Hatch, J. R., 1989, Geochemistry of Oils and Hydrocarbon Source Rocks, Greater Anadarko Basin; Evidence For Multiple Sources of Oils and Long-Distance Oil Migrations, Oklahoma Geological Survey Circular, No. 90, pp. 53-64.

Calf, F. E. and Habermehl, M. A., 1983 Isotope Hydrology and Hydrochemistry of the Great Artesian Basin, Australia, *in*: Isotope Hydrology 1983, pp. 397-413, Int. At. Energy Agency, Vienna.

Carpenter, A. B., 1978, Origin and chemical evolution of brines in sedimentary basins, Oklahoma Geological Survey Circular 79, pp. 60-70.

Cathles, L . M. III., 1990, Scales and effects of fluid flow in the upper crust, Science, Vol. 248, Issue No. 4953, pp. 323-329.

Chaudhuri, S., Broedel, V., and Clauer, N., 1987, Strontium isotopic composition of oil-field waters from carbonate reservoir rocks in Bindley field, central Kansas, U.S.A., Geochimica et Cosmochimica Acta, Vol. 51, pp. 45-53.

Chaudhuri, S., and Clauer, N., 1993, Strontium isotopic compositions and potassium and rubidium contents of formation waters in sedimentary basins: Clues to the origin of the solutes, Geochimica et Cosmochimica Acta, Vol. 57, pp. 429-437.

Chaudhuri, S., Robinson, R., Clauer, N., and Jones, L. M., 1992, Evolution of formation waters in Early Pennsylvanian Morrowan sandstones in the Hugoton Embayment of the Anadarko Basin, southern Midcontinent, U.S.A., Oklahoma Geological Survey Circular 93, pp. 160-174.

Clark, J. F., Davisson, M. L., Hudson, G. B., and Macfarlane, P. A., 1998, Noble Gases, Stable Isotopes and Radiocarbon as Tracers of Flow in the Dakota Aquifer, Colorado and Kansas, Journal of Hydrology, Vol. 211, pp. 151-167.

Clayton, R. N., Friedman, I., Graf, D. L., Mayeda, T. K., Meents, W. F., and Shimp, N. F., 1966, The Origin of Saline Formation Waters. 1. Isotopic Composition, J. Geophys. Res., Vol. 71, pp. 3869-3882

Craig, H., 1961, Isotopic Variations in Meteoric Waters, Science, Vol. 133, pp. 1702-1703.

Dansgaard, W., 1964, Stable isotopes in precipitation, Tellus, Vol. 16, pp. 436-468.

Darton, N. H., 1905, Preliminary report on the geology and underground water resources of the central Great Plains, USGS Professional Paper, 433 p.

Davis, S. N., Campbell, D. J., Bentley, H. W., and Flynn, T. J., 1985, Ground Water Tracers, National Water Well Association, Worthington, Ohio, 199 p.

Davisson, M. L. and Criss, R E., 1996, Na-Ca-Cl relations in basinal fluids, Geochimica et Cosmochimica Acta, Vol. 60, No. 15, pp. 2743-2752.

Dutton, A. R., 1994, Sources and ages of ground water in unconfined and confined aquifers beneath the U.S. high plains, Final technical report, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas.

Dutton, A. R., 1995, Groundwater Evidence for Paleorecharge in U.S. High Plains Aquifers, Quaternary Research, Vol. 43, pp. 221-231.

Dutton, A. R. and Bein, A, 1993, Origin, distribution, and movement of brine in the Permian Basin (U.S.A.): A model for displacement of connate brine, GSA Bulletin, Vol. 105, pp. 695-707.

Epstein, S., and Mayeda, T.K., 1953, Variations of O^{18} contents of waters from natural sources, Geochimica and Cosmochimica Acta, Vol. 4, pp. 213-224.

Faure, G., 1986, Principles of isotope geology, 2nd Edition, 589 p. John Wiley & Sons publishers

Franz, R. H., 1985, Distribution of petrophysical properties in the lower Morrow sandstone (Keyes), southwest Kansas *in:* Watney, W. L., and Doveton, J. H., Core studies in Kansas, Kansas Geol. Surv. Subsurface Geol. Series, No. 6 pp. 56-65.

Garven, G., 1985, The role of regional fluid flow in the genesis of the Pine Point Deposit, Western Canada sedimentary basin, Economic Geology and the Bulletin of Economic Geologists, Vol. 80, Issue 2, pp. 307-324.

Giletti, B. J. and Casserly, J. E. D., 1994, Strontium diffusion kinetics in plagioclase feldspars, Geochimica et Cosmochimica Acta, Vol. 58, No. 18, pp. 3785-3793.

Girard, P., Hillaire-Marcel, C., and Oga, M. S., 1997, Determining the Recharge Mode of Sahelian Aquifers Using Water Isotopes, Journal of Hydrology, Vol. 197, pp. 189-202.

Gogel, T., 1981, Discharge of saltwater from Permian rocks to major stream-aquifer systems in central Kansas, Kansas Geological Survey, Chemical Quality Series No. 9, 60 p.

Gosselin, D., Harvey, F. E., and Frost, C. D., 2001, Geochemical Evolution of Ground Water in the Great Plains (Dakota) Aquifer of Nebraska: Implications for the Management of a Regional Aquifer system, Ground Water, Vol. 39, No. 1, pp. 98-108.

Gosselin, D. C., Harvey, E. F., Forst, C. D., Stotler, R. and Macfarlane, P. A., 2004, Strontium Isotope Geochemistry of Groundwater in the Central part of the Dakota (Great Plains) Aquifer, USA, Applied Geochemistry, Vol. 19, pp. 359-377.

Grobe, M., and Machel, H. G., 2002, Saline groundwater in the Münsterland Cretaceous Basin, Germany: Clues to its origin and evolution, Marine and Petroleum Geology, Vol., 19, pp. 307-322.

Gunter, W. D., Perkins, E. H., and Hutcheon, I., 2000, Aquifer Disposal of Acid Gases: Modeling of Water-Rock Reactions for Trapping of Acid Wastes, Applied Geochemistry, Vol. 15, pp. 1085-1095.

Hanor, J. S., 1987, Origin and migration of subsurface sedimentary brines, SEPM Short Course No. 21, 247 p.

Hanor, J. S., 1983, Fifty years of development of thought on the origin and evolution of subsurface sedimentary brines: *in* Boardman, S. J. (ed.), Revolution in the Earth Sciences, Kendal Hunt Publishing Co., pp. 99-111.

Helgesen, J. O., and Leonard, R. B., 1988, Geohydrology of the Great Plains aquifer system, central United States *in:* Swain, L. A, and Johnson, A. I., (eds.), 1988, Regional Aquifer systems of the United States, Aquifers of the Midwestern area, AWRA Monograph series No. 13, pp. 179-190.

Helgesen, J. O., Leonard, R. B., and Wolf, R. U., 1993, Hydrology of the Great Plains Aquifer System in Nebraska, Colorado, Kansas, and adjacent areas, USGS Professional Paper, 1414-E.

Hetherington, E. A., Stueber, A. M., and Pushkar, P., 1986, Strontium isotopic study of subsurface brines from Illinois Basin (Abstr.), Amer. Assoc. Petrol. Geol. Bull. Vol. 70, p. 600.

Hitchon, B., and Friedman, I., 1969, Geochemistry and Origin of Formation Waters in the Western Canada Basin – I Stable Isotopes of Oxygen and Hydrogen, Geochimica et Cosmochimica Acta, Vol. 33, pp. 1321-1349.

Holdoway, K. A., 1978, Deposition of evaporites and red beds of the Nipewalla Group, Permian, western Kansas, Kansas Geol. Survey Bull., No. 215, 43p.

Holser, W. T., 1979, Mineralogy of evaporites *in*: Burns, R. G. (ed.), 1979, Mineralogical Society of America short course notes, Vol. 6, pp. 211-294.

Horita, J., Bencoe, J. G., and Cole, D. R., 2001, Fundamental geochemical research on long term carbon sequestration in subsurface, AAPG Expanded Abstracts, June 2001, pp. 92.

Jorgensen, D. G., 1989, Paleohydrology of the Anadarko Basin, Central United States, Oklahoma Geological Survey Circular No. 90, 176-193.

Jorgensen, D. G., Helgesen J. O., and Imes, J. L., 1993, Regional aquifers in Kansas, Nebraska, and parts of Arkansas, Colorado, Missouri, New Mexico, Oklahoma, south Dakota, Texas and Wyoming-geohydrologic framework, USGS Professional Paper 1414-B.

Jorgensen, D. G, and Signor, D. C., (eds.), 1984, Geohydrology of the Dakota aquifer, Proceedings of the First C. V. Theis conference on geohydrology; geohydrology of the Dakota aquifer. Lincoln, NE, Oct. 5-6, 1982, 247 p.

Jorgensen, D. G., Leonard, R. B., Signor, D. C., and Helgesen, J. O, 1986a, Midwest Regional Aquifer Study: Regional Aquifer System Analysis Program of the USGS, USGS Circular 1002, pp. 132-140.

Kloppmann, W., Négrel Ph., Cassanova, J., Klinge, H., Schelkes, K., and Guerrot, C., 2001, Halite Dissolution derived brines in the vicinity of a Permian salt dome (N. Germany Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes, Geochimica et Cosmochimica Acta, Vol. 65, No. 22, pp. 4087-4101.

Knauth, L. P. and Beeunas, M. A., 1986, Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters, Geochimica et Cosmochimica Acta, Vol. 50, pp. 419-433.

Land, L. S., 1987, The major ion chemistry of saline brines in sedimentary basins *in:* Banavar, J. R., Koplik, J., and Winkler, K. W., eds., International Symposium on Physics and Chemistry of Porous Media, 2nd, Ridgefield, Connecticut, 1986, Proceedings, New York, American Institute of Physics, No. 154, pp. 160-179.

Land, L. S., 1995, Na-Ca-Cl Saline formation waters, Frio Formation (Oligocene), South Texas, USA: Products of diagenesis, Geochimica et Cosmochimica Acta, Vol 59, No. 11, pp. 2163-2174.

Land, L. S., and Macpherson, G. L., 1992, Origin of saline formation waters, Cenozoic section, Gulf of Mexico Sedimentary Basin, AAPG Bulletin, Vol. 76, No. 9, pp. 1344-1362.

Land, L. S., and Prezbindowski, D, R., 1981, The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A., Journal of Hydrology, Vol. 54, pp. 51-74.

Larson, T. G., 1971, Hydrodynamic Relationships in the Mid-Continent *in*: Cram, I. H. (ed) Future Petroleum Provinces of the Mid-Continent – Their Geology and Potential, AAPG Memoir 15, Vol. 2, pp. 1043-1046.

Lopes, T. J. and Hoffman, J. P., 1997, Geochemical Analyses of Ground-Water Ages, Recharge Rates, and Hydraulic Conductivity of the N Aquifer, Black Mesa Area, Arizona, USGS Water Resources Investigations Report 96-4190.

Macfarlane, P. A., 1995, The effect of river valleys and the Upper Cretaceous aquitard on regional flow in the Dakota aquifer in the central Great Plains of Kansas and southeastern Colorado, Kansas Geological Survey Bulletin, Vol. 238, pp. 11-30.

Macfarlane, P. A., Clark, J. F., Davisson, M. L., Hudson, G. B., and Whittemore, D. O., 2000, Late-Quaternary Recharge Determined from Chloride in Shallow Groundwater in the Central Great Plains, Quaternary Research, Vol. 53, pp. 167-174.

Macfarlane, P. A., Förster, A, Merriam, D. F., Schrötter, J., and Healy, J. M., 2002, Monitoring Artificially Stimulated Fluid Movement in the Cretaceous Dakota Aquifer, Western Kansas, Hydrogeology Journal, Vol. 10, pp. 662-673.

Mazor, E., 1991, Applied Chemical and Isotopic Groundwater Hydrology, Halsted Press, 274 p.

McCaffrey, M. A., Lazar, B., and Holland, H. D., 1987, The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite, Journal of Sedimentary Petrology, Vol. 57, No. 5, pp. 928-937.

Mearns, E. W., and McBride, J. J., 1999, Hydrocarbon Filling History and Reservoir Continuity of Oil Fields Evaluated using $^{87}Sr/^{86}Sr$ Isotope Ratio Variations in Formation Water, with Examples from the North Sea, Petroleum Geoscience, Vol. 5, pp. 17-27.

Miller, A., and Appel, C. L., 1997, Ground water atlas of the United States, Kansas, Missouri, and Nebraska, USGS, HA 730-D.

Musgrove, M., 1993, Origin, evolution, and mixing of saline and dilute groundwaters in three regional flow systems, Midcontinent, U.S.A., unpub. M.S., The University of Texas at Austin, 225 p.

Musgrove, M., and Banner, J. L., 1993, Regional ground-water mixing and the origin of saline fluids: Midcontinent, United States, Science, Vol. 259, pp. 1877-1882.

Musgrove, M., and Banner, J. L., 2004, Controls on the spatial and temporal variability of vadose dripwater geochemistry; Edwards Aquifer, central Texas, Geochimica et Cosmochimica Acta, Vol. 68, Issue 5, pp. 1007-1020.

Nicastro, L., 1983, Isotopic and chemical studies of oil-field waters associated with Upper Paleozoic rocks, Miner field, Ness County, Kansas, unpub. M.S., Kansas State University, 89 p.

Orr, W. L., 1974, Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-study of Big Horn basin Paleozoic oils, AAPG, Vol. 58, No. 11, pp. 2295-2318.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE; a computer program for geochemical calculations, Water Resources Investigations, USGS, WRI 80-96, 216 p. s

Pierre, C., Ortlieb, L., and Person, A., 1984, Supratidal evaporitic dolomite at Ojo de Liebre lagoon: mineralogical and isotopic arguments for primary recrystallization, Jour. of Sed. Petrol., Vol. 54, No. 4, pp. 1049-1061.

Plummer, L. N., Prestemon, E. C., and Parkhurst, D. L., 1991, An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, USGS Water Resources Investigation Report 91-4078, 227 p.

Robinson, T. J., Chaudhuri, S., and Jones, L. M., 1985, Diagenesis of Pennsylvanian Morrowan sandstones, Clark county, Kansas *in:* Watney, W. L., and Doveton, J. H., Core studies in Kansas, Kansas Geol. Surv. Subsurface Geol. Series, No. 6 pp. 56-65.

Siegel, D. I., and Mandle, R. J., 1984, Isotopic Evidence for Glacial Meltwater Recharge to the Cambrian-Ordovician Aquifer, North-Central United States, Quaternary Research, Vol. 22, pp. 328-335.

Siegel, D. I., 1989, Geochemistry of the Cambrian-Ordovician Aquifer System in the Northern Midwest, United States, USGS Professional Paper 1405-D, 76 p.

Signor, D. C., 1988, Regional flow systems in the central United States, GSA Abstracts with Program 20, No. 2, p. 129.

Signor, D. C., and Imes, J. L., 1988, Geohydrology of regional aquifer systems in Cretaceous and older rocks underlying the central U.S.: *in* Swain, L. A., and Johnson, I.A., Regional aquifer systems of the United States, aquifers of the midwestern area, AWRA Monograph Series No. 13.

Solomon, D.K., Cook, P.G. and Sanford, W.E., 1998, Dissolved Gases in Subsurface Hydrology. In: C. Kendall and J.J. McDonnell (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, pp. 291-318.

Sunwall, M. T., Pushkar, P., 1979, The isotopic composition of strontium in brines from petroleum field of southeastern Ohio, Chem. Geol. Vol. 24, pp. 189-197.

Stueber, A. M., Pushkar, P., and Hetherington, E. A., 1987, A strontium isotopic study of formation waters from the Illinois Basin, U.S.A., Appl. Geochemistry, Vol. 2, pp. 477-494.

Swenson, F. A., 1968, New theory of recharge to the artesian basin of the Dakotas, GSA Bulletin, Vol. 79, Issue 2, pp. 163-182.

Taylor, H. P., Jr., 1974, The Application of Oxygen and Hydrogen Isotope Studies to Problems of Hydrothermal Alteration and Ore Deposition, Econ. Geol., Vol. 69, pp. 843-883.

Torgensen, T., Habermehl, M. A., Phillips, F. M., Elmore, D., Kubik, P., Jones, B. G., Hemmick, T., and Gove, H. E., 1991, Chlorine 36 Dating of Very Old Groundwater 3. Further Studies in the Great Artesian Basin, Australia, Water Resources Research, Vol. 27, No. 12, pp. 3201-3213.

Tóth, J., 1995, Hydraulic Continuity in Large Sedimentary Basins, Hydrogeology Journal, Vol. 3, No. 4, pp. 4-16.

Walter, L. M., Stueber, A. M., and Huston, T. J., 1990, Br-Cl-Na systematics in Illinois Basin fluids: Constraints on fluid origin and evolution, Geol., Vol. 18, pp. 315-318.

Webb, T., III, and Bryson, R. A., 1972, Late and Postglacial Climatic Change in the Northern Midwest, U.S.A.: Quaternary Estimated Derived from Fossil Pollen

Spectra by Multivariate Statistical Analysis, Quaternary Research, Vol. 2, pp. 70-113.

Wilson, T.P., and Long, D. T., 1993, Geochemistry and isotope chemistry of the Michigan basin brines: Devonian formations, Applied Geochemistry, Vol. 8, pp. 81-100.

Worden, R. H, Coleman, M. L., and Matray, J-M, 1999, Basin scale evolution of formation waters: A diagenetic and formation water study of the Triassic Chaunoy Formation, Paris Basin, Geochimica et Cosmochimica Acta, Vol. 63, No. 17, pp. 2513-2528.

Yapp, C. J., and Epstein, S., 1977, Climatic Implications of D/H Ratios of Meteoric Waters over North America (9,500-22,000 b.p.) as Inferred from Ancient Wood Cellulose C-H Hydrogen, Earth Planetary Science Letters, Vol. 34, pp. 330-350.

Vita

Rosario Vasquez Scheerhorn was born in the New York, New York in August 10, 1967, the daughter of Cesar Vasquez and Maria Isabel Carlota Saenz de Vasquez. After residing in New York for a couple of years her family moved back to Buenos Aires, Argentina. She completed her high school degree from Nuestra Señora de la Unidad high school in Buenos Aires in 1985. She studied anthropology at the University of Buenos Aires for 3 years. After 3 years, due to the political situation in Argentina, she decided to go abroad finish her college carrer. From 1988 to May 1989 she attended DePauw University in Buenos Aires, while she still attended the University of Buenos Aires, In August 1989 she came to USA to finish her degree in anthropology at DePauw University in Greencastle, Indiana. She received her degree of Bachelor of Arts from DePauw in May 1992 , with a double major in Geology and Anthropology. Seeking for warmer weather, she entered Baylor University in Waco, Texas where she received her Masters of Science in Geology in 1994. Her MS was on conodont paleoecology and biostratigraphy. She is currently employed by ConocoPhillips working on reservoir quality, seal analysis, and water-rock interaction.

In May 1996 she married Jeff Scheerhorn and on January 1, 2000 they had their first child Oliver Cesar Scheerhorn and on 2003 their second son, Lorenzo Alexander Scheerhorn was born.

Permanent address: 5919 Bayonne Dr., Spring, TX 77389

This dissertation was typed by Rosario Vasquez Scheerhorn